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I. MESYL ESTERS OF GLYCEROL^{1,2}

BY ERICH BAER AND ALAN G. NEWCOMBE³

Abstract

The syntheses of L- α -monomesylin^{4,5}, D- α,β - and DL- α,β -dimesylin, and trimesylin are described and some of their physical properties are reported. It was observed that the optical rotations of L- α -monomesylin and D- α,β -dimesylin in pyridine solutions change with time, whereas the rotations of the same compounds in the sterically hindered base, 2,6-lutidine, remain constant. Of the two previously reported values for the refraction of the $-O-SO_2-$ group the value of Tasker and Purves was confirmed. The mono- and dimesylins form the starting materials for the syntheses of the diacyl L- α -monomesylins and the acyl D- α,β -dimesylins.

Introduction

During the past 14 years methods have been developed in this Laboratory which permit the syntheses of the pure enantiomeric forms of asymmetrically substituted glycerol derivatives of predetermined constitution and configuration. These methods have been applied mainly to the preparation of lipids and phospholipids. It was felt that it would be of interest to extend our studies to the field of the sulphonic acid esters of glycerol as well. It was decided to prepare the following four mesyl esters, namely, L- α -monomesylin, DL- and D- α,β -dimesylin, and trimesylin. The syntheses are illustrated by reaction schemes A, B, and C.

The optical purity of the L- α -monomesylin was established by converting it into dipalmitoyl L- α -monomesylin and distearoyl L- α -monomesylin and preparing these compounds also by an independent method. The rotations of the corresponding mixed acid triglycerides were, within experimental error, identical. The optical purity of the D- α,β -dimesylin was established in a similar manner. The syntheses of these mixed acid triglycerides will be described in a subsequent paper.

¹ Manuscript received June 25, 1951.

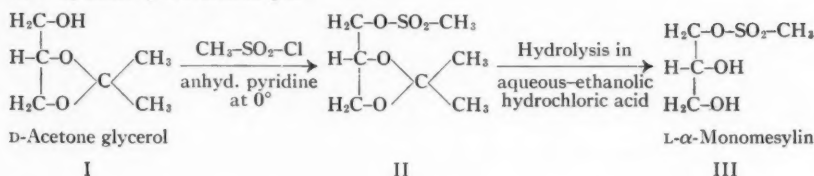
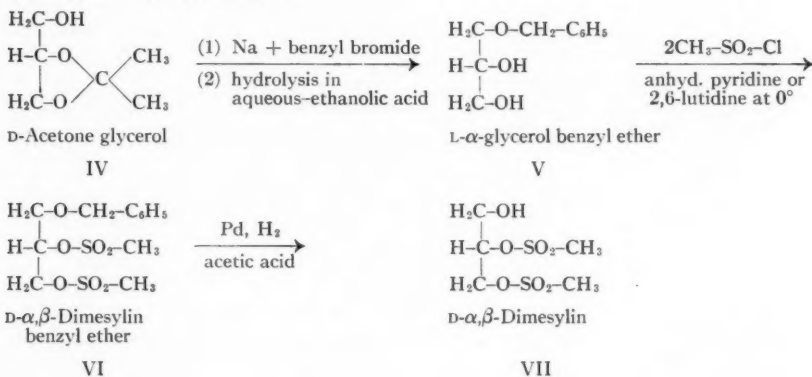
Contribution from the Banting and Best Department of Medical Research, Banting Institute, Toronto, Ont. This paper forms part of a thesis submitted by A. G. Newcombe to the Department of Chemistry of the University of Toronto, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, May, 1950.

² The use of "mesyl", instead of "methanesulfonyl-", was suggested by Helferich and Gnüchtel (9) and is followed here.

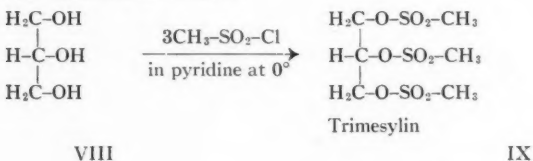
³ Recipient of a scholarship from the Research Council of Ontario, 1948-1949, and from the National Research Council of Canada, summer, 1949.

⁴ In conformity with the nomenclature applied to the glycerol esters of fatty acids, monomesyl glycerol, dimesyl glycerol, and trimesyl glycerol will be called monomesylin, dimesylin, and trimesylin, respectively.

⁵ With regard to the optical classification of asymmetrically substituted glycerol derivatives see Fischer, H. O. L. and Baer, E. *Chem. Revs.* 29: 295, 299. 1941.

(A) Synthesis of L- α -monomesylin*(B) Synthesis of D- α , β -dimesylin*

(C) Synthesis of trimesylin



REACTION SCHEMES

* The use of L- or DL-acetone glycerol as starting material yields D- α - or DL- α -monomesylin and L- α , β - or DL- α , β -dimesylin, respectively.

It was observed that the optical rotations of pyridine solutions of L- α -monomesylin and D- α , β -dimesylin changed with time (see Table I). The fact that the optical rotation of a solution of D- α , β -dimesylin in 2,6-lutidine, a sterically hindered base (5), was constant over a period of nine days suggests that the change of rotation in pyridine solution is caused by the formation of the glyceryl pyridinium mesylates of both the dimesylin and the monomesylin. This type of reaction has been observed by Ferns and Lapworth (6) to occur rapidly with ethyl tosylate and pyridine. The possibility that the change of rotation in pyridine was caused by the elimination of methanesulphonic acid, resulting in the formation of an epoxy-ring, was considered, but seems to be unlikely since the strongly basic 2,6-lutidine could be expected to act like pyridine in removing the methanesulphonic acid.

The possession of four new liquid mesyl esters was a challenge to re-determine the molecular refraction of the $-O-SO_2-$ group for which two values have been reported. The average value of 10.44 ± 0.27 found by us is in good agreement with that found by Tasker and Purves (11) 10.53 ± 0.35 , but varies slightly from that reported by Whitmore and Landau (12), 9.7 ± 0.2 .

Experimental

D-Acetone Glycerol

L- α -MONOMESYLIN

This substance was prepared according to the method of Baer and Fischer (2) by the catalytic reduction of acetone D-glyceraldehyde at atmospheric pressure (4) and was obtained in an average yield of 70%. $[\alpha]_D^{24} = +13.7^\circ$ in substance. $n_D^{22} = 1.4360$.

Monomesyl D-Acetone Glycerol

To an ice-cold solution of 17.7 gm. (0.134 mole) of D-acetone glycerol in 75 ml. of anhydrous pyridine, protected against the intrusion of moisture, was added slowly and with agitation 15.3 gm. (0.134 mole) of mesyl chloride. The solution was allowed to stand at 0° for a period of 17 hr. At the end of this time crushed ice and a slurry of 11.3 gm. (0.134 mole) of sodium bicarbonate in 40 ml. of water was added to the reaction mixture. After concentrating the solution under reduced pressure, the residue, consisting of solid sodium chloride and a pale yellow oil, was treated with 100 ml. of anhydrous ether and the ether extract was cleared by centrifugation (ether extract I). The sodium chloride and undissolved oil was then treated with a mixture of 125 ml. of anhydrous ether and 125 ml. of 99% ethanol, and the extract, after freeing from sodium chloride, was concentrated *in vacuo* to a thick oil. The oil was dissolved in anhydrous ether, freed from traces of sodium chloride, and combined with ether extract I. The extracts were decolorized with activated charcoal and concentrated under reduced pressure. The residual oil was then fractionally distilled *in vacuo*, using a flask with sealed-on receiver (1). The fraction boiling from 91 to 93° (0.07 mm.) weighed 23.9 gm. (84.9% of theory) and was pure monomesyl D-acetone glycerol. $[\alpha]_D^{24} = -8.0^\circ$ in substance; $[\alpha]_D^{28} = -7.4^\circ \pm 0.1^\circ$ in 95% ethanol (*c*, 7); $n_D^{15.5} = 1.4555$, $n_D^{21} = 1.4535$, $n_D^{25} = 1.4520$, $d^{15.5} = 1.2470$, $d^{21} = 1.2409$, $d^{25} = 1.2370$. Calc. for $C_7H_{14}O_5S$ (210.24): C, 39.98; H, 6.71; S, 15.25; acetone, 27.6%. Found: C, 39.88; H, 6.70; S, 14.96; acetone, 27.5%.

L- α -Monomesylin

A solution of 5.1 gm. (0.0243 mole) of monomesyl D-acetone glycerol in 150 ml. of 95% ethanol and 30 ml. of 0.5 *N* hydrochloric acid was allowed to stand at room temperature. The rotation of the solution was determined from time to time and was found to become constant at the end of 12 hr. After standing for a total of 18 hr. the mixture was made neutral to litmus by the addition of an aqueous solution of sodium bicarbonate and concentrated

under reduced pressure. The mixture of oil and solid sodium chloride was treated with several portions of 99% ethanol, and the combined extracts were concentrated *in vacuo*. The residue, which still contained sodium chloride, was treated with five 80 ml. portions of anhydrous ether, and the combined extracts were again concentrated under reduced pressure. The residual oil was freed of solvent and moisture in a high vacuum over phosphorus pentoxide. In this manner 3.45 gm. (83.4% of theory) of L- α -monomesylin was obtained. Attempts to distill the monomesylin *in vacuo* resulted in the decomposition of the material. $n_D^{15} = 1.4580$, $n_D^{25} = 1.4553$, $d^{15} = 1.370$, $d^{25} = 1.358$. Calc. for $C_4H_{10}O_5S$ (170.18): C, 28.23; H, 5.92%. Found: C, 28.13; H, 6.19%. $[\alpha]_D^{29} = -14.1^\circ$ in anhydrous pyridine (c, 10). $[\alpha]_D^{30} = -12.7^\circ \pm 0.3^\circ$ in 0.001 N sulphuric acid (c, 11). $[\alpha]_D^{30} = -8.6^\circ \pm 0.3^\circ$ in glacial acetic acid (c, 10). $[\alpha]_D^{29} = -9.3^\circ \pm 0.2^\circ$ in 90% acetic acid (c, 11). $[\alpha]_D^{32} = -15.7^\circ \pm 0.5^\circ$ in a solvent consisting of 8.3 ml. of 95% ethanol and 1.7 ml. of 0.5 N hydrochloric acid (c, 12). The reported specific rotations are those observed shortly after preparing the solutions. The rotation of the L- α -monomesylin in 90% acetic acid, the de-acetonation mixture, or 0.001 N sulphuric acid remained constant for at least two, three, or six days, respectively. However, in pyridine the rotation increased, becoming more and more negative (Table I), while in glacial acetic acid the rotation decreased, becoming zero in the course of one week.

TABLE I

Days	L- α -Monomesylin in pyridine (c, 10) $[\alpha]_D^{22-27}$	D-Dimesylin in pyridine (c, 9) $[\alpha]_D^{22-27}$	D-Dimesylin in 2,6-lutidine (c, 10) $[\alpha]_D^{22-27}$
0	$-14.0^\circ \pm 0.2^\circ$	$+2.1^\circ \pm 0.2^\circ$	$+6.1^\circ \pm 0.2^\circ$
1	15.0 0.5		
2	16.0 0.2		
3			5.8 0.2
5			5.7 0.1
6	18.9 0.4	3.0 0.2	
9	21.3 0.3	3.5 0.1	+6.2 0.1
10	22.0 0.2		
11	22.7 0.6		
12	23.5 0.6		
13	24.2 0.2		
14		3.6 0.1	
16	26.6 0.4		
19	28.7 0.6		
23	31.4 0.6		
27		+4.1 0.2	
30	35.0 0.6		
40	41.3 0.1		
49	42.4 0.1		
143	-75.0 0.2		

Vicinal-Glycol Titration with Lead Tetraacetate in Aqueous Acetic Acid

Five milliliter aliquots of a 0.0348 M solution of L- α -monomesylin in 50% acetic acid were mixed each with a 20 ml. portion of an approximately 0.015 M solution of lead tetraacetate in glacial acetic acid and the consumption of lead

tetraacetate was determined at stated intervals. At the end of 2.5, 6.33, 6.66, 21.0, 21.5, 41.0, and 44.5 hr., 0.562, 0.764, 0.764, 0.992, 0.983, 0.996, and 1.03 moles, respectively, of lead tetraacetate per one mole of monomesylin had been consumed. According to the final consumption of lead tetraacetate the monomesylin was the pure α -isomer.

The periodate oxidation of the L- α -monomesylin in dilute (8×10^{-2} or 8×10^{-4} N) sulphuric acid proceeded in an anomalous fashion consuming 1.95 moles of periodate in the course of two hours.

D- AND DL- α,β -DIMESYLIN

The L- α - and DL- α -benzyl glycerol ethers were prepared by the slightly modified (4) procedure of Sowden and Fischer (10).

D- α,β -Dimesylin Benzyl Ether

To a solution of 4.53 gm. (0.0248 moles) of L- α -benzyl glycerol ether in 30 ml. of anhydrous pyridine was added dropwise and with cooling 5.69 gm. (0.0497 moles) of mesyl chloride. After standing overnight at 0°C. the solution was poured into 500 ml. of ice water and the D-dimesylin benzyl ether was extracted with three 175 ml. portions of ether. The combined ether extracts were washed twice with 200 ml. of ice-cold 0.5 N sulphuric acid, twice with 200 ml. of saturated aqueous sodium bicarbonate solution, and twice with water. The ether solution was then dried over anhydrous sodium sulphate, filtered, and concentrated under diminished pressure. The residual oil after being completely freed from solvent *in vacuo* (0.1 mm.) weighed 7.05 gm. (84% of theory) and was pure D-dimesylin benzyl ether. $n_D^{20} = 1.5156$; $d^{20} = 1.338$; $d^{25} = 1.328$; $[\alpha]_D^{26} = +8.72^\circ \pm 0.23^\circ$ in anhydrous chloroform (c , 8.6), $[M]_D = +29.5^\circ \pm 0.9$. Calc. for $C_{12}H_{18}O_7S_2$ (338.38): C, 42.59; H, 5.36%. Found: C, 42.63; H, 5.32%.

In an experiment which was identical with the foregoing except that anhydrous 2,6-lutidine (30 ml.) was used in place of pyridine, 92% of the theoretical amount of the α -benzyl ether of D-dimesylin was obtained. $[\alpha]_D^{26} = +8.72^\circ \pm 0.12^\circ$ (c , 8.8 in anhydrous chloroform).

DL- α,β -Dimesylin Benzyl Ether

Prepared as described for the D-isomer. Yield 85% of theory. $n_D^{20} = 1.5161$; $n_D^{25} = 1.5142$; $n_D^{30} = 1.5128$. Calc. for $C_{12}H_{18}O_7S_2$ (338.38): C, 42.59; H, 5.36%. Found: C, 42.71; H, 5.36%.

D- α,β -Dimesylin

A freshly prepared solution of 5.0 gm. (0.0148 mole) of D-dimesylin benzyl ether in 35 ml. of glacial acetic acid together with 1.0 gm. of palladium catalyst was vigorously shaken at room temperature in an atmosphere of hydrogen at an initial pressure of approximately 50 cm. of water, until the consumption of hydrogen ceased (30 min.). After displacing the hydrogen with nitrogen,

the mixture was centrifuged and the catalyst was washed first with 99% ethanol and then with anhydrous ether. The combined solutions were concentrated under reduced pressure and the residue freed *in vacuo* (0.01 mm. Hg) from organic solvents and moisture. The D-dimesylin weighed 3.29 gm. (89.6% of theory) and was analytically pure. $[\alpha]_D^{26} = +3.36^\circ \pm 0.1^\circ$ in anhydrous pyridine (*c*, 9). $n_D^{20} = 1.4698$, $n_D^{25} = 1.4681$, $d^{20} = 1.438$, $d^{25} = 1.440$. Calc. for $C_5H_{12}O_7S_2$ (248.27): C, 24.19; H, 4.87%. Found: C, 24.11; H, 4.82%.

Columns 2 and 3 of Table I report the specific rotations exhibited by the pyridine and 2,6-lutidine solutions of D- α,β -dimesylin on standing at room temperature. It is of interest to note that the rotation of the lutidine solution remains constant whereas that of the pyridine solution changes considerably with time.

DL- α,β -Dimesylin

This compound was prepared by the catalytic hydrogenolysis of DL- α,β -dimesylin benzyl ether according to the procedure described above. The DL- α,β -dimesylin was obtained in almost theoretical yield. Calc. for $C_5H_{12}O_7S_2$ (248.27): C, 24.19; H, 4.87%. Found: C, 24.31; H, 4.86%.

TRIMESYLIN

To the ice-cold solution of 1.01 gm. (0.011 mole) of glycerol dissolved in 10 ml. of anhydrous pyridine was added dropwise 4.4 gm. (0.038 mole) of mesyl chloride. After standing 22 hr. at 0° , approximately 40 gm. of crushed ice was added to the bright red solution and the mixture was placed overnight in an ice box ($+6^\circ$). The almost colorless precipitate was filtered off and washed thoroughly with water. The crude material was recrystallized from warm acetone by the addition of ether and yielded 3.04 gm. (86% of theory) of pure trimesylin, m.p. $79-81^\circ$. The trimesylin is soluble in water at 25° to the extent of 0.21 gm. in 100 ml. of solution. Calc. for $C_6H_{14}O_9S_3$ (326.35): C, 22.08; H, 4.32; S, 29.47%. Found: C, 22.09; H, 4.24; S, 29.46%.

Molecular Refraction of the $-O-SO_2-$ Group

The molecular refraction of the $-O-SO_2-$ group was obtained by deducting from the experimentally found molecular refractions of mesyl D-acetone glycerol, L- α -monomesylin, D- α,β -dimesylin benzyl ether, and DL- α,β -dimesylin the calculated molecular refractions of their $-O-SO_2-$ free moieties (Table II). The Lorentz-Lorenz equation and Eisenlohr's (8) atomic refractions were used in these calculations. The atomic refraction of the two oxygen atoms in the five-membered heterocyclic ring of mesyl D-acetone glycerol was assumed to have the same value as hydroxyl-oxygen (1.525). This value agrees fairly well with that (1.515) calculated by us, from the molecular refraction reported by E. Fischer and Pfähler (7) for acetone glycerol.

TABLE II
 MOLECULAR REFRACTION OF THE $-O-SO_2-$ GROUP

Compound	<i>n</i>	<i>d</i>	M.R. found	M.R. calculated for the $-O-SO_2-$ -free moieties	$-O-SO_2-$ group refraction
Mesityl D-acetone glycerol	15°	15°			
	1.4555	1.247	45.79	35.38	10.41
	21°	21°			
	1.4535	1.241	45.84		10.46
L- α -monomesylin	25°	25°			
	1.4521	1.237	45.86		10.48
	15°	15°			
	1.4580	1.370	33.90	23.72	10.17
D-dimesylin benzyl ether	25°	25°			
	1.4553	1.358	34.02		10.30
	20°	20°			
	1.5161	1.338	76.41	55.66	10.37
DL- α,β -dimesylin	25°	25°			
	1.5142	1.328	76.51		10.54
	20°	20°			
	1.4698	1.438	48.16	26.82	10.67
	25°	25°			
	1.4681	1.440	47.93		10.56
					Aver. value = 10.44 \pm 0.27

Acknowledgments

One of the authors (A.G.N.) wishes to express his sincerest appreciation to the Research Council of Ontario and to the National Research Council of Canada for scholarships received during the years 1948-1949 and 1949, respectively.

References

1. BAER, E. *Ind. Eng. Chem. Anal. Ed.* 16: 399. 1944.
2. BAER, E. and FISCHER, H. O. L. *J. Biol. Chem.* 128: 463. 1939.
3. BAER, E. and KATES, M. *J. Am. Chem. Soc.* 70: 1394. 1948.
4. BAER, E. and KATES, M. *J. Am. Chem. Soc.* 72: 942. 1950.
5. BROWN, H. C., SCHLESINGER, H. I., and CARDON, S. Z. *J. Am. Chem. Soc.* 64: 325. 1942.
6. FERNS, J. and LAPWORTH, A. *J. Chem. Soc.* 101: 273. 1912.
7. FISCHER, E. and PFÄHLER, E. *Ber.* 53: 1606. 1920.
8. GLASSTONE, S. *Text-book of physical chemistry*. 1st ed. D. van Nostrand Co., New York. 1943. p. 520.
9. HELFERICH, B. and GNÜCHTEL, A. *Ber.* 71: 712. 1938.
10. SOWDEN, J. C. and FISCHER, H. O. L. *J. Am. Chem. Soc.* 63: 3244. 1941.
11. TASKER, C. W. and PURVES, C. B. *J. Am. Chem. Soc.* 71: 1017. 1949.
12. WHITMORE, W. F. and LANDAU, E. F. *J. Am. Chem. Soc.* 68: 1797. 1946.

ASYMMETRICALLY SUBSTITUTED MIXED ACID TRIGLYCERIDES

ACYL DERIVATIVES OF L- α -MONOMESYLIN AND D- α,β -DIMESYLIN¹

BY ERICH BAER AND ALAN G. NEWCOMBE

Abstract

As part of a general program concerning the synthesis of the enantiomeric forms of asymmetrically substituted glycerol derivatives, dipalmitoyl and distearoyl L- α -monomesylin, and palmitoyl and stearoyl D- α,β -dimesylin were prepared. With the exception of stearoyl D- α,β -dimesylin, each of the mixed acid triglycerides was synthesized by two independent procedures. The individual triglyceride, regardless of the method of synthesis, was obtained with the same rotation, thus assuring the optical purity not only of the mixed acid triglycerides but also of L- α -monomesylin and D- α,β -dimesylin.

Introduction

The monoacyl D- α,β -dimesylins and diacyl L- α -monomesylins were prepared by two independent methods, (a) the mesylation of L- α -monopalmitin, L- α -monostearin, D- α,β -dipalmitin, and D- α,β -distearin, respectively, as shown by Equations A and C, and (b) by the acylation of D- α,β -dimesylin and L- α -monomesylin according to Equations B and D, using stearoyl and palmitoyl chloride.

The desired products were obtained by both methods with identical rotations thus assuring the optical purity not only of the monoacyl dimesylins and diacyl monomesylins but also of monomesylin and dimesylin. Of the two methods of synthesis the first (a) is preferable to the second (b) since it offers less preparative difficulties and the yields were found to be considerably higher.

During previous work in this laboratory (2,7) it was observed that with increasing substitution of glycerol by long chain, normal, fatty acids (monoglycerides \rightarrow diglycerides \rightarrow triglycerides) the optical activity of the asymmetric glycerides decreases and becomes unobservable in the triglycerides but reappears and increases considerably in magnitude (7,8,9) with the stepwise introduction of aromatic acids. Similar, although not as striking, increases in optical activity have now been observed with the introduction of mesyl substituents in the mixed acid triglycerides.

In making the stereochemical assignments for the mixed acid triglycerides the mesyl glyceride moieties were chosen as compounds of reference, since the mesyl group is common to all of them. This follows the precedent set by this laboratory in choosing the stereochemical moiety of reference for the α -lecithins (4), α -cephalins (5), and α -phosphatidic acids (1). Thus the mixed acid

¹ Manuscript received June 25, 1951.

Contribution from the Banting and Best Department of Medical Research, Banting Institute, Toronto, Ont. This paper forms part of a thesis submitted by A. G. Newcombe to the Department of Chemistry of the University of Toronto, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, May, 1950.

triglycerides containing the D-forms of the mesyl glycerides are considered to be members of the D-series and vice versa. The steric classification of the mono- and dimesylins is established unambiguously by relating these compounds to the glyceraldehydes,² the compounds of stereochemical reference, *via* acetone glycerol and acetone glyceraldehyde.

Experimental

Stearoyl D- α , β -Dimesylin (By Mesylation of Monostearin)

To an ice-cold solution of 3.58 gm. (0.01 mole) of L- α -monostearin (2,3) in 40 ml. of anhydrous pyridine was added slowly and with exclusion of moisture 3.44 gm. (0.03 mole) of mesyl chloride, and the mixture was kept at 0° for 18 hr. At the end of this time 70 gm. of crushed ice was added and the precipitate was collected with suction on a Büchner funnel, washed thoroughly with water, and dried *in vacuo* over phosphorus pentoxide. For purification the crude material was reprecipitated from hot acetone by the addition of 95% ethanol and by cooling to +6°. The stearoyl D- α , β -dimesylin was obtained in the form of colorless needles and in a yield of 98% (5.05 gm.). This material sintered to a viscous and translucent liquid from 72.5° to 75.0° and formed a meniscus at 89°. For further purification the substance was recrystallized from benzene by the addition of 95% ethanol and by cooling to +6°. The resultant stearoyl D- α , β -dimesylin (4.25 gm., 83%) started to sinter at 71.5°, formed a viscous, translucent liquid from 75.5–76.5°, and developed a meniscus at 91°. $[\alpha]_D^{26} = -3.3^\circ \pm 0.2^\circ$ in anhydrous chloroform (*c*, 10). $[\alpha]_D^{26} = -4.4^\circ \pm 0.1^\circ$ in anhydrous pyridine (*c*, 10). Calc. for C₂₃H₄₆O₈S₂ (514.7): C, 53.66; H, 9.01; S, 12.46%. Found: C, 53.22; H, 8.93; S, 12.19%.

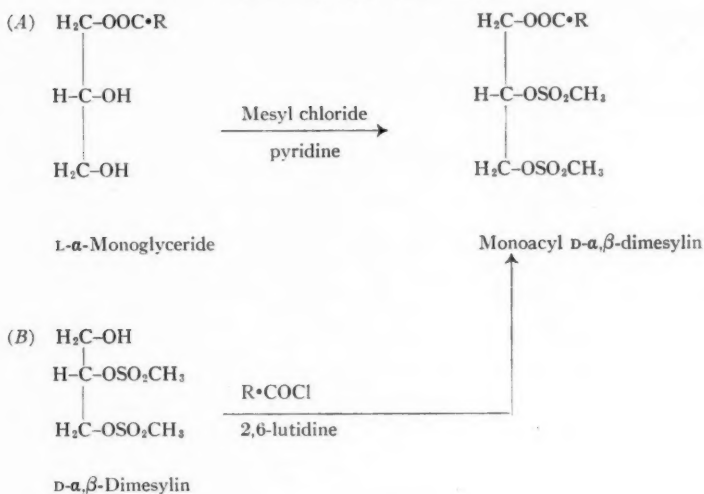
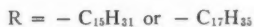
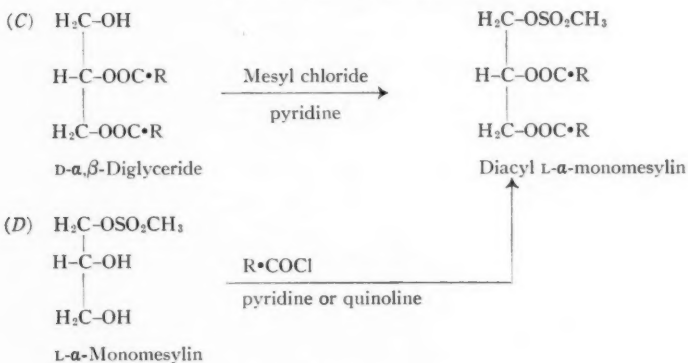
Stearoyl DL- α , β -Dimesylin

Prepared as described for the optically active compound, starting, however, with DL- α -monostearin (6). The stearoyl DL- α , β -dimesylin, which was obtained in a yield of 98%, sintered to a viscous, translucent liquid at 67–70° and formed a meniscus at 88°. It was insoluble in cold water, ethanol, or cyclohexane, and fairly soluble in cold benzene, or dioxane. It was also fairly soluble in boiling ether, acetone, dioxane, or cyclohexane and readily soluble at room temperature in chloroform, benzene, or pyridine. Calc. for C₂₃H₄₆O₈S₂ (514.7): C, 53.66; H, 9.01; S, 12.46%. Found: C, 53.33; H, 8.86; S, 12.37%.

Palmitoyl D- α , β -Dimesylin (By Mesylation of Monopalmitin)

Prepared as described for the corresponding stearoyl compound, starting with L- α -monopalmitin (2,3). The crude reaction product sintered at 65.0°, formed a viscous, translucent liquid at 70° and developed a meniscus at 77°. It was recrystallized by dissolving in boiling acetone, diluting the solution

² With regard to the steric classification and nomenclature of glycerides see Fischer, H. O. L. and Baer, E. *Chem. Revs.* 29: 287, 299. 1941.

Synthesis of Acyl D- α , β -DimesylinSynthesis of Diacyl L- α -Monomesylin

with 95% ethanol, and by cooling to $+6^\circ$. The pure palmitoyl D- α , β -dimesylin which was obtained in a yield of 88.5%, sintered at 69.5° , formed a viscous, translucent liquid at 71.5 to 72.5° and developed a meniscus at 78.5° . Further recrystallizations did not change the melting point. $[\alpha]_D^{26} = -4.8^\circ \pm 0.1^\circ$ in anhydrous pyridine³ (*c*, 10); $[\alpha]_D^{25} = -3.5^\circ \pm 0.1^\circ$ in anhydrous chloroform (*c*, 10). Calc. for $\text{C}_{21}\text{H}_{42}\text{O}_8\text{S}_2$ (486.7): C, 51.83; H, 8.69; S, 13.18%. Found: C, 51.41; H, 8.65; S, 13.15%.

³ Unchanged after nine days.

Palmitoyl DL- α,β -Dimesylin

Prepared and purified as described for the optically active compound above, starting, however, with DL- α -monopalmitin (6). The palmitoyl DL- α,β -dimesylin, which was obtained in a yield of 78%, sintered to a viscous, translucent liquid from 60.5 to 62.5° and formed a meniscus at 77.5°. Calc. for $C_{21}H_{42}O_8S_2$ (486.7): C, 51.83; H, 8.69; S, 13.18%. Found: C, 51.56; H, 8.71; S, 13.08%.

Palmitoyl D- α,β -Dimesylin (By Acylation of Dimesylin)

To a suspension of 2.48 gm. (0.01 mole) of D-dimesylin⁴ in 12 ml. of anhydrous carbon tetrachloride and 2.3 ml. (0.02 mole) of 2,6-lutidine, was added a solution of 2.75 gm. (0.01 mole) of palmitoyl chloride in 8 ml. of anhydrous carbon tetrachloride and the mixture, protected against moisture, was kept at 40°. At the end of 40 hr. the reaction mixture was poured with stirring into a mixture of 100 ml. of ether and 100 ml. of water. The precipitate was centrifuged down, washed thoroughly with water, and, after drying *in vacuo*, recrystallized twice from small volumes of hot acetone by the addition of 95% ethanol and cooling to + 6°. The colorless palmitoyl D- α,β -dimesylin, which was obtained in a yield of 21.4% (1.04 gm.), sintered at 68.0°, formed a viscous, translucent liquid at 70.0°, and developed a meniscus at 76.0°. $[\alpha]_D^{25} = -4.8^\circ \pm 0.2^\circ$ in anhydrous pyridine (*c*, 10). Calc. for $C_{21}H_{42}O_8S_2$ (486.7): C, 51.83; H, 8.69%. Found: C, 51.76; H, 8.68%.

Distearoyl L- α -Monomesylin (By Mesylation of Distearin)

To a solution of 1.25 gm. (0.002 mole) of D-distearin (4,9) in a mixture of 20 ml. of anhydrous ether and 12 ml. of anhydrous pyridine was added at room temperature and under anhydrous conditions 0.46 gm. (0.004 mole) of mesyl chloride. The reaction mixture was allowed to stand at room temperature for 17 hr. At the end of this period crushed ice was added, the mixture was filtered, and the white precipitate, after drying thoroughly, was recrystallized from 50 ml. of acetone. The substance was obtained in the form of fine, colorless needles which melted from 71.2 to 74.0°. Subsequent recrystallizations, first from 50 ml. of a mixture of chloroform and petroleum ether (1:7; v/v) and then from 55 ml. of acetone, yielded a product which melted from 73.5–75.4°. The pure distearoyl L- α -monomesylin was obtained in a yield of 66% (0.93 gm.). $[\alpha]_D^{23} = +1.6^\circ \pm 0.1^\circ$ in anhydrous chloroform (*c*, 7). Calc. for $C_{40}H_{78}O_7S$ (703.1): C, 68.33; H, 11.18; S, 4.56%. Found: C, 68.45; H, 11.31; S, 4.72%.

Distearoyl DL- α -Monomesylin

Prepared as described for the optically active compound, starting, however, with DL- α,β -distearin (4). The distearoyl DL- α -monomesylin, which was obtained in a yield of 63%, melted at 75.0–76.0°. Calc. for $C_{40}H_{78}O_7S$ (703.1): C, 68.33; H, 11.18; S, 4.56%. Found: C, 68.10; H, 11.00; S, 4.63%.

⁴ See preceding paper in this issue.

Distearoyl L- α -Monomesylin (By Acylation of Monomesylin)

To a solution of 0.85 gm. (0.005 mole) of L- α -monomesylin⁴ in 7.5 ml. of anhydrous quinoline was added with cooling and under anhydrous conditions a solution of 3.03 gm. (0.01 mole) of stearoyl chloride in 5.0 ml. of anhydrous quinoline, and the mixture was allowed to stand for four days at room temperature. At the end of this time the reaction mixture was taken up in 100 ml. of ether and 150 ml. of 0.5 *N* hydrochloric acid. After separating the two phases, the ether layer was washed in rapid succession with 150 ml. of 0.5 *N* hydrochloric acid, 100 ml. of water, 100 ml. of a saturated sodium bicarbonate solution, and again with 50 ml. of water. All operations were carried out in the cold. The ether extract was dried over anhydrous sodium sulphate and evaporated to dryness *in vacuo*. The hot acetone solution (55 ml.) of the residue, after treating with activated charcoal, yielded, on cooling to +6°, colorless distearoyl L- α -monomesylin which, after further recrystallizations from, (a) chloroform - petroleum ether, (b) acetone, (c) chloroform - petroleum ether, melted from 72.5 to 74.2°. Yield 15% of theory (0.54 gm.). $[\alpha]_D^{25} = +1.7^\circ \pm 0.2^\circ$ in anhydrous chloroform (c, 10). Calc. for C₄₀H₇₈O₇S (703.1): C, 68.33; H, 11.18%. Found: C, 68.45; H, 11.05%.

Dipalmitoyl L- α -Monomesylin (By Mesylation of Dipalmitin)

The substance was prepared as described for the corresponding stearoyl compound. The mesylation of D- α,β -dipalmitin (4,9) (2.84 gm., 0.005 mole) by means of mesyl chloride (1.15 gm., 0.01 mole) in pyridine (25 ml.) and recrystallization of the crude reaction product from acetone (60-80 ml.), then from 120 ml. of a mixture of chloroform and petroleum ether (1:7; v/v), yielded 2.56 gm. (79%) of pure dipalmitoyl L- α -monomesylin, melting from 68.5-70.0°. $[\alpha]_D^{25} = +1.7^\circ \pm 0.2^\circ$ in anhydrous chloroform (c, 8); $[\alpha]_D^{25} = +2.4^\circ \pm 0.1^\circ$ in anhydrous pyridine³ (c, 10). Calc. for C₃₈H₇₀O₇S (647.0): C, 66.83; H, 10.91; S, 4.95%. Found: C, 66.83; H, 10.58; S, 5.13%.

Dipalmitoyl DL- α -Monomesylin

This substance was prepared in the same manner as the L-isomer. The mesylation of 2.84 gm. (0.005 mole) of DL- α,β -dipalmitin (4) yielded 3.04 gm. (94%) of pure, crystalline dipalmitoyl DL- α -monomesylin, melting at 67.0-68.5°. Calc. for C₃₈H₇₀O₇S (647.0): C, 66.83; H, 10.91; S, 4.95%. Found: C, 66.92; H, 10.85; S, 4.92%.

Dipalmitoyl L- α -Monomesylin (By Acylation of Monomesylin)

To a solution of 0.85 gm. (0.005 mole) of L- α -monomesylin⁴ in 12 ml. of anhydrous pyridine was added with cooling and exclusion of moisture 2.75 gm. (0.01 mole) of palmitoyl chloride. After standing at room temperature for one day, the solid mass was triturated with 12 ml. of anhydrous carbon tetrachloride and allowed to stand for a further five days. At the end of this period the dark red reaction mixture was poured onto a mixture of crushed ice, water, and chloroform. The chloroform solution was washed consecutively with

two portions of 180 ml. each of ice-cold 0.5 *N* sulphuric acid, water, saturated sodium bicarbonate solution, and again with water, and after drying with anhydrous sodium sulphate, was evaporated to dryness under reduced pressure. The dark brown solution of the residue in 100 ml. of warm acetone was decolorized with activated charcoal and cooled in ice. The crude product (0.49 gm., 15%), after recrystallization from 20 ml. of a mixture of chloroform and petroleum ether (v/v; 1:7) followed by recrystallization from 35 ml. of acetone, yielded 0.32 gm. (10%) of pure dipalmitoyl *L*- α -monomesylin, m.p. 66.5–68.5°. $[\alpha]_D^{25} = +1.8^\circ \pm 0.3^\circ$ in anhydrous chloroform (*c*, 6). Calc. for $C_{36}H_{70}O_7S$ (647.0): C, 66.83; H, 10.91%. Found: C, 66.44; H, 11.10%.

Acknowledgments

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References

1. BAER, E. *J. Biol. Chem.* 189: 235. 1951.
2. BAER, E. and FISCHER, H. O. L. *J. Biol. Chem.* 128: 475. 1939.
3. BAER, E. and FISCHER, H. O. L. *J. Am. Chem. Soc.* 67: 2031. 1945.
4. BAER, E. and KATES, M. *J. Am. Chem. Soc.* 72: 942. 1950.
5. BAER, E., MAURUKAS, J., and RUSSELL, M. *Science*, 113: 12. 1951.
6. FISCHER, E., BERGMANN, M., and BÄRWIND, H. *Ber.* 53: 1599. 1920.
7. FISCHER, H. O. L. and BAER, E. *Naturwissenschaften*, 25: 588. 1937.
8. FISCHER, H. O. L. and BAER, E. *Chem. Revs.* 29: 287. 1941.
9. FISCHER, H. O. L. and SOWDEN, J. C. *J. Am. Chem. Soc.* 63: 3244. 1941.

IONIC SPECIES IN CERIC PERCHLORATE SOLUTIONS¹

BY T. J. HARDWICK AND E. ROBERTSON

Abstract

Ceric ion has been shown to exist in perchloric acid solution as a mixture of Ce^{4+} , CeOH^{3+} , and a dimer, probably $(\text{Ce-O-Ce})^{6+}$. From a spectral study between 395 and 430 $\text{m}\mu$, the values of the equilibrium ratios have been determined, along with the molar extinction coefficients of each ion over this region of wave length. The thermodynamic quantities ΔH , ΔF° , and ΔS° have been determined for each reaction.

Introduction

Recently Heidt and Smith (2) postulated the existence of a stable dimer of cerium in ceric perchlorate solution. This assumption enabled them to explain some unusual effects observed in the photochemical reduction of ceric ion in perchloric acid. Kolp and Thomas (3) believed that the thermal reduction of ceric perchlorate in aqueous solution could best be explained by the existence of a stable dimer of cerium.

On the other hand, Smith (7) maintained that tetravalent cerium exists as $\text{Ce}(\text{ClO}_4)_4$ in perchloric acid solution. Moore and Anderson (5) in their spectral study of the ceric sulphate complexes, omitted consideration of the possibility of dimerization of ceric ion.

A number of papers have been published on the potential of the ceric-cerous couple in perchloric acid solutions (6, 7) but the data therein shed no light on the question of dimer existence.

It appeared that the most promising way to investigate the existence of dimer was to make a detailed spectral study of ceric perchlorate - perchloric acid solutions. If a dimer is formed, Beer's law will not be followed. At high ceric ion concentrations the apparent molar extinction coefficient should decrease, as the total number of absorbing species actually present is decreased. A change in absorption with changing acid concentration indicates the presence of one or more hydrolysis products of the ceric ion.

Experimental

Materials

Ceric perchlorate solution: This was prepared essentially by the method used by Sherrill (6). C.P. ammonium ceric sulphate (G. Frederick Smith Co.) was dissolved in dilute nitric acid and reduced to the cerous state by hydrogen peroxide. Cerous oxalate was precipitated and washed free from sulphate. The precipitate was dissolved in nitric acid and fumed down successively in hydrochloric and perchloric acids. The resulting syrup was diluted to give a cerium

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concentration of 0.56 *M* and an acid concentration of 2.7 *M*. Negative tests were obtained for nitrate, chloride, and sulphate. Portions of this solution were oxidized electrolytically, about 95% conversion being achieved. This was the stock solution from which all dilutions were made.

Perchloric acid: 4.00 *M* solutions were prepared from Merck's Reagent 70% acid.

Sodium hydroxide: 4.00 *M* solutions were made from Nichol's Reagent sodium hydroxide.

Preparation of Solutions

The stock solutions were kept in a room maintained at $25 \pm 1^\circ\text{C}$. Appropriate dilutions were made using the stock ceric solution, the acid, and the alkali to give solutions of the required ceric ion concentration, acidity, and ionic strength. The volume of solution made was 25 ml.

Analysis of Solutions

Perchloric acid solutions were standardized against dilute sodium hydroxide; sodium hydroxide solutions against standard hydrochloric acid prepared by the constant boiling method. Cerium analysis was carried out as follows: an aliquot of ceric solution was added to a slight excess of standard ferrous ion in dilute sulphuric acid solution. The excess ferrous ion was determined colorimetrically by the *o*-phenanthroline method. Duplicate analyses were made on a ceric solution before and after a series of spectral measurements. No change was ever noticed in the time interval. Analytical error was in all cases less than 0.4%.

Optical Measurements

The instrument used was a Beckman Photoelectric Quartz Spectrophotometer. A special cell holder housing was made which allowed water at $25.00 \pm 0.05^\circ\text{C}$. to circulate through the walls of the cell compartment.

The solutions to be investigated were immersed in a bath at $25.00 \pm 0.01^\circ\text{C}$. for at least one hour before use. In making measurements three "corex" cells of 1 cm. path length were used—one containing a blank of perchloric acid—sodium perchlorate solution appropriate to the ceric solution, and the other two the test solution. The cells were placed in the instrument and the per cent transmission measured from 395 $m\mu$ to 430 $m\mu$ in steps of 5 $m\mu$.

Results

A small amount of cerous ion was invariably present in all samples, arising from incomplete oxidation of stock cerium solution and/or autoredox of ceric ion during dilution. However, under the conditions used in these experiments, cerous ion does not absorb light and can therefore be omitted from consideration.

The transmission of ceric perchlorate solutions was measured under the following conditions:

Series	Range of ceric ion concentration	$[H^+]$	Γ
A	$1.3 - 13.0 \times 10^{-3} M$	0.20	2.00
B	$0.7 - 12.5 \times 10^{-3} M$	1.00	2.00
C	$1.3 - 13.6 \times 10^{-3} M$	2.00	2.10
D	$6.5 \text{ and } 9.2 \times 10^{-3} M$	1.00	1.10-4.00

where Γ is the molar ionic strength. The results of A, B, and C appear in Fig. 1, those of D in Fig. 3.

Discussion

The apparent molar extinction coefficients will be defined by:

$$\bar{\epsilon} = \frac{1}{C} \log \frac{I_0}{I} \text{ (for unit path length)} \quad (1)$$

$$= \frac{D}{C} \quad (1a)$$

where C is the total concentration of tetravalent cerium, I_0 and I are the intensities of light passing through the blank and test solutions respectively, and D is the optical density of the solution. Fig. 1 shows a plot of $\bar{\epsilon}$ vs. C for various hydrogen ion concentrations at different wave lengths.

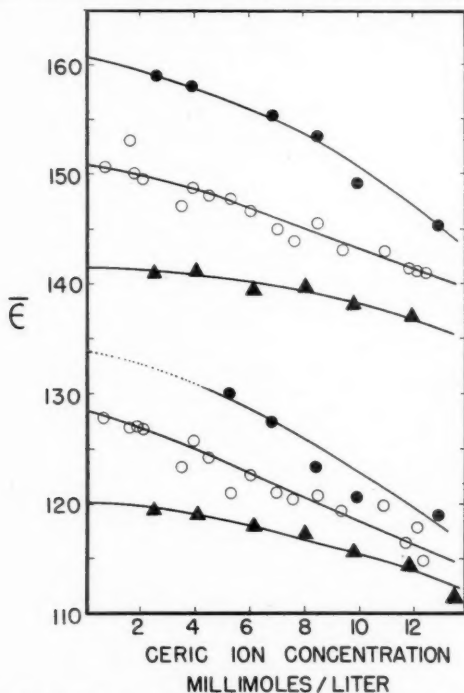
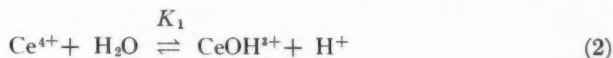


FIG. 1. Apparent molar extinction coefficients as a function of ceric ion concentration. Upper set: $\lambda = 400 m\mu$. Lower set: $\lambda = 405 m\mu$.

● $[H^+] = 0.20 N$, ○ $[H^+] = 1.00 N$, ▲ $[H^+] = 2.00 N$

Two features of these data are noteworthy. First, an increase in acid concentration results in a decreased value of $\bar{\epsilon}$. This shows that an equilibrium involving H^+ or OH^- must be present. Heidt (2) has postulated the equilibrium,



$$K_1 = \frac{[CeOH^{3+}][H^+]}{[Ce^{4+}]} \quad (3)$$

Let M = the concentration of $CeOH^{3+}$ at equilibrium,

X = the concentration of Ce^{4+} at equilibrium,

C = the total concentration of tetravalent cerium in solution, then

$$K_1 = \frac{M[H^+]}{X} \quad (3a)$$

$$= \frac{(C - X)[H^+]}{X} \quad (3b)$$

$$X = \frac{C[H^+]}{K_1 + [H^+]} \quad (4)$$

$$D = \epsilon_x X + \epsilon_m (C - X) \quad (5)$$

$$= \epsilon_x \frac{C[H^+]}{K_1 + [H^+]} + \epsilon_m \frac{CK_1}{K_1 + [H^+]} \quad (5a)$$

where ϵ_x and ϵ_m are the molar extinction coefficients for Ce^{4+} and $CeOH^{3+}$ respectively.

For every value of C , the data allow three equations in the unknowns, ϵ_x , ϵ_m , and K_1 to be set up—one for each acid concentration. These equations may be reduced to the form

$$K_1 D_{1,2,3} - C(K_1 \epsilon_m) - C[H^+]_{1,2,3} = -D_{1,2,3} [H^+]_{1,2,3} \quad (5b)$$

By considering $K_1 \epsilon_m$ an unknown constant instead of ϵ_m , a solution to these equations may be obtained. The values of $\bar{\epsilon}$ at $C = 1.0 \times 10^{-3} M$ and $\lambda = 400 m\mu$ were used in calculating K_1 . This result ($K_1 = 5.2$) was used to calculate ϵ_m and ϵ_x values at all wave lengths. Calculations of K_1 from data at longer wave lengths gives rise to a large probable error, as the differences between the $\bar{\epsilon}$ values are very small.

Two assumptions have been made in these calculations. First, only one hydrolysis form of ceric ion is considered present, i.e., $CeOH^{3+}$. The formation of $Ce(OH)_2^{2+}$ is not excluded, but such an ion, if present, would either exist in small amounts or possess a spectrum very much similar to that of $CeOH^{3+}$. Second, the pair of ions related by hydrolysis is considered to be $Ce^{4+} - CeOH^{3+}$. This could equally well be $CeOH^{3+} - Ce(OH)_2^{2+}$ as far as mathematical interpretation of the work is concerned. However, with zirconium in 2 M perchloric acid, the average number of hydroxyl ions associated with zirconium is between zero and one (1); with uranous ion in 2 M perchloric acid, *ca.* 98% is found to

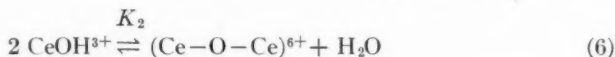
be in the U^{4+} state (4). From this work one calculates only 28% present as unassociated Ce^{4+} ions in 2 *M* perchloric acid. It is therefore quite likely that the hydrolysis couple $Ce^{4+} - CeOH^{3+}$ is the one involved.

The value of $\bar{\epsilon}$ for a particular acid concentration varies when *C* varies. As will be demonstrated later, this is caused by the formation of a dimer of $CeOH^{3+}$. The true values for K_1 , ϵ_x and ϵ_m should be calculated at $C \rightarrow 0$. However, as extrapolation to zero would lead to significant inaccuracies, the calculations were made at $C = 1.0 \times 10^{-3}$ *M*, at which concentration the proportion of dimer is rather small. Small corrections (amounting to about 1%) were subsequently made to ϵ_x and ϵ_m for dimer; K_1 was found not to change. The corrected values are recorded in Table I and are plotted against wave length in Fig. 2.

TABLE I
MOLAR EXTINCTION COEFFICIENTS

λ m μ	Ce^{4+} ϵ_x	$CeOH^{3+}$ ϵ_m	Dimer ϵ_p
395	100	192	
400	85.5	163	210
405	72	138.5	137
410	61.5	117.5	100
415	53	99.5	70
420	48	83	47.5
425	43.5	69.5	33.5
430	40.5	58	5.7

The second feature of the curves in Fig. 1 is the decrease in $\bar{\epsilon}$ as *C* increases at constant acidity and ionic strength. This can be explained only by assuming some kind of polymerization of ceric ion. Heidt (2) has suggested that $CeOH^{3+}$ dimerizes.



$$K_2 = \frac{[(Ce-O-Ce)^{6+}]}{[CeOH^{3+}]^2} \quad (7)$$

For convenience let *P* = the concentration of $(Ce-O-Ce)^{6+}$ at equilibrium with all other symbols as before. The concentration of dimer will be

$$P = \frac{1}{2} \{C - (M + X)\} \quad (8)$$

$$\text{also } D = \epsilon_x X + \epsilon_m M + \epsilon_p P \quad (9)$$

Substituting Equations (3a) and (8) in Equation (9) one obtains

$$M = \frac{D - \frac{1}{2} \epsilon_p C}{\epsilon_x \frac{[H^+]}{K_1} + \epsilon_m - \frac{1}{2} \epsilon_p \left(\frac{[H^+]}{K_1} + 1 \right)} \quad (10)$$

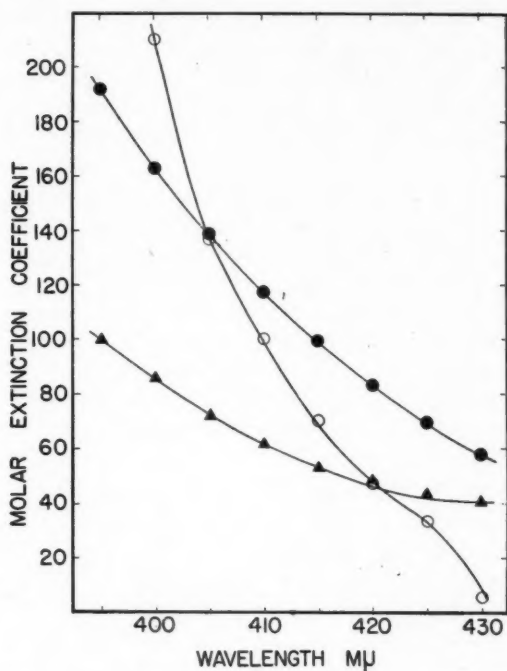


FIG. 2. Spectra of the species present in ceric perchlorate solution.
 ▲ Ce^{3+} , ● $CeOH^{3+}$, ○ dimer

Once M is known, X is obtained from Equation (3a), P from Equation (8) and K_2 from Equation (7). Equation (10) contains two unknowns, M and ϵ_p . However, by choosing low acid concentrations and high cerium concentrations, X becomes relatively negligible and P a significant fraction of the total cerium. Equation (10) then reduces to

$$M = \frac{D - \frac{1}{2}\epsilon_p C}{\epsilon_m - \frac{1}{2}\epsilon_p} \quad (10a)$$

The fraction of the total cerium remaining as $CeOH^{3+}$ is

$$\frac{M}{C} = \frac{\bar{\epsilon} - \frac{1}{2}\epsilon_p}{\epsilon_m - \frac{1}{2}\epsilon_p} \quad (10b)$$

By successive approximations one can calculate values of ϵ_p at different wavelengths which give a constant value of M/C . One can now substitute these ϵ_p values in Equation (10) to determine M using data from the smoothed curve

values of $\bar{\epsilon}$ for $[H^+] = 1$. By successive approximations one obtains good values for K_2 and ϵ_p ; ϵ_p values are recorded in Table I and are plotted against wave length in Fig. 2. K_2 was found to be 16.5. These extinction coefficients and equilibrium ratios were used to calculate $\bar{\epsilon}$ values. A comparison with the measured ones at 0.2 and 2.0 *M* acid showed an agreement better than $\pm 0.5\%$ in most cases.

We have been able to interpret the decrease in $\bar{\epsilon}$ with increasing ceric ion concentration only by assuming that an equilibrium exists between ceric ion and a dimer of ceric ion. The evidence for the existence of this dimer seems quite conclusive, as the calculation of the optical density of a solution (using the constants found in this work) agrees with measured values within 1%. We do not agree with the conclusions of Moore and Anderson that ceric perchlorate solutions obey Beer's law up to concentrations of 0.01 *M*. Reactions of this type have been demonstrated to occur in uranous and zirconium salt solutions (1). It appears that the higher the valence of the ion, the greater the tendency to polymerize.

The chemical form of the dimer may be $(Ce-O-Ce)^{6+}$ or some hydrolyzed form such as $(HO-Ce-O-Ce)^{5+}$ or $(HO-Ce-O-Ce-OH)^{4+}$. As the apparent extinction coefficient of the dimer is the same for all the acid concentrations studied, we can conclude only that the form of the dimer is the same between 0.2 *M* and 2.0 *M* acid, or that the absorption spectra of the various forms are quite similar.

Effect of Ionic Strength on the Equilibria

K_1 and K_2 , like all equilibrium ratios involving ions, depend upon ionic strength. In the preceding work, Γ has been kept constant at 2.00 or 2.10. Fig. 3 shows the effect of changing ionic strength on $\bar{\epsilon}$ for two ceric ion concentrations. The acid was maintained at 1.0 *M* and the ionic strength changed by the addition of sodium perchlorate.

The invariance of $\bar{\epsilon}$ with ionic strength is interpreted to mean that the values of the equilibrium ratios do not change with changes in ionic strength. This may be explained by assuming that the changes in activity coefficients of the ions in Equations (3) and (7) cancel numerically. This will hold true more for K_1 than K_2 , as small changes in K_2 would not be noticeable under the conditions used.

The perchlorate ion concentration is increased fourfold with no resultant increase in $\bar{\epsilon}$. It is therefore quite unlikely that any equilibrium involving perchlorate ions is set up.

Effect of Temperature on the Equilibria

In order to investigate the effect of temperature on the $Ce^{4+} - CeOH^{3+}$ equilibrium, conditions were chosen such that dimer concentration would be low and have little effect on the optical density of the system. A solution where

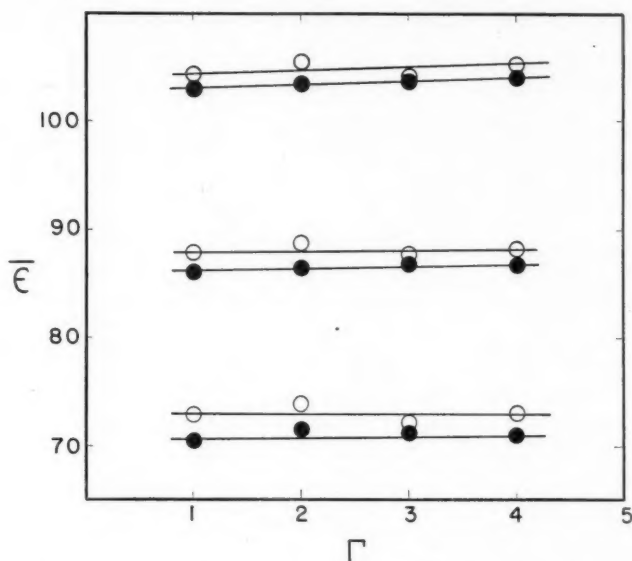


FIG. 3. Effect of molar ionic strength on the apparent molar extinction coefficient for $\lambda = 410$, 415, and 420 m μ .

- $[Ce^{IV}] = 9.2 \times 10^{-3}$ moles/liter
 ● $[Ce^{IV}] = 6.3 \times 10^{-3}$ moles/liter

$[H^+] = 2.0 M$, $\Gamma = 2.1$, total ceric ion $= 2.0 \times 10^{-3} M$ was used. The optical densities of this solution were measured between 430 and 395 m μ at 5, 15, 25, and 35°C. The values of X and subsequently K_1 at the different temperatures were found using a modified form of Equation (5).

$$\frac{X}{C} = \frac{\epsilon_m - \bar{\epsilon}}{\epsilon_m - \epsilon_x} \quad (5c)$$

The mean values of K_1 at each temperature are recorded in Table II and are plotted against $1/T$ in Fig. 4. From the slope of this curve one calculates $\Delta H = 15.5 \pm 1$ kcal. for the first hydrolysis of Ce^{4+} .

TABLE II
EFFECT OF TEMPERATURE ON ASSOCIATION CONSTANTS

Temp., °C.	K_1	K_2
5	0.87	110
15	2.1	41.5
25	5.2	16.5
35	15.0	3.1

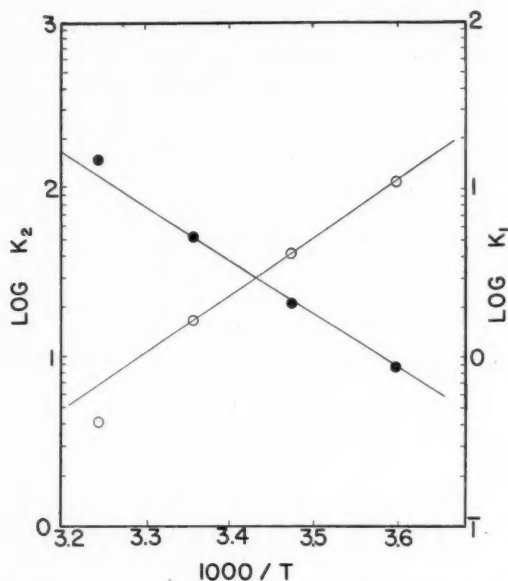


FIG. 4. Equilibrium ratios as a function of temperature.
 ○ K_2 values. ● K_1 values.

By choosing the following conditions: $[H^+] = 0.2 M$, $\Gamma = 2.0$, $[Ce^{IV}]_0 = 1.10 \times 10^{-2} M$, only small amounts of Ce^{4+} are present, while dimer is in as large a concentration as is feasible under the conditions of the work. The optical densities of the above solutions were measured over the previous wave length range at temperatures of 5, 15, 25, and 35°C. From Equations (10), (3a), (8), and (7) one obtains the value of K_2 . The mean values of K_2 at each temperature are recorded in Table II and are plotted against $1/T$ in Fig. 4. From the slope of this curve one calculates $\Delta H = -16 \pm 1$ kcal. for the formation of dimer from $CeOH^{3+}$.

Thermodynamic Constants

Using the Equation $\Delta S = R \ln K + \frac{\Delta H}{T}$ the entropy change may be found

for the reactions. The free energy and entropy changes are for

	Hydrolysis	Dimerization
ΔF° kcal.	- 3.1	- 1.7
ΔS° e.s.u.	55.4	- 48.3

By adding the corresponding values for the neutralization reaction, one obtains the thermodynamic constants for the association reaction proper.

	ΔH kcal.	ΔF° kcal.	ΔS° e.s.u.
$Ce^{4+} + H_2O \rightarrow CeOH^{3+} + H^+$	15.5	- 3.1	55.4
$H^+ + OH^- \rightarrow H_2O$	- 13.5	-19.1	19
$Ce^{4+} + OH^- \rightarrow CeOH^{3+}$	2.0	- 22.2	74.4

Migration Experiments

A qualitative migration experiment was made to determine the nature of the charge on the ions in solution. A three compartment cell with fine sintered glass partitions was used (Fig. 5). In the center compartment a ceric perchlorate solution was placed ($[Ce^{IV}] = 10^{-2} M$, $[H^+] = 1.0 N$, $\Gamma = 2.0$) and in the outer compartments an appropriate perchloric acid - sodium perchlorate solution, all liquid levels being made equal. Migration was determined by the appearance of color in the outer compartments.

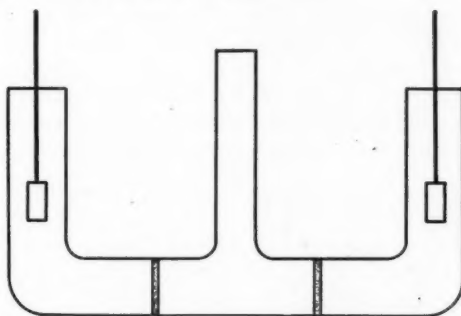


FIG. 5. Three compartment diffusion cell.

No natural migration occurred in 24 hr. Application of 67 1/2 v. at the electrode caused migration of color to the cathode, none to the anode. Reversal of electrode polarity reversed the direction of migration. Thus ceric perchlorate solutions contain positive and no negative ceric ions or complexes. Neutral species are not detectable.

References

1. CONNICK, R. E. and McVEY, W. H. J. Am. Chem. Soc. 71: 3182. 1948.
2. HEIDT, L. J. and SMITH, M. E. J. Am. Chem. Soc. 70: 2476. 1948.
3. KOLP, D. and THOMAS, H. C. J. Am. Chem. Soc. 71: 3047. 1949.
4. KRAUS, K. A. and NELSON, F. ORNL-23. 1948.
5. MOORE, R. L. and ANDERSON, R. C. J. Am. Chem. Soc. 67: 167. 1945.
6. SHERRILL, M. S., KING, C. B., and SPOONER, R. C. J. Am. Chem. Soc. 65: 170. 1943.
7. SMITH, G. F. Cerate oxidimetry. The G. Frederick Smith Chemical Co., Columbus, Ohio. pp. 93-95. 1942.

ASSOCIATION OF CERIC IONS WITH SULPHATE (A SPECTRAL STUDY)¹

BY T. J. HARDWICK AND E. ROBERTSON

Abstract

Ceric ion has been shown to associate with sulphate ion to form successively $\text{Ce}(\text{SO}_4)^{++}$, $\text{Ce}(\text{SO}_4)_2$, and $\text{Ce}(\text{SO}_4)_3^-$. The association constants relating these species have been determined at 25°C. The molar extinction coefficients of each associated complex have been found between 395 and 430 m μ . Migration experiments bear out the results qualitatively.

There is considerable evidence of complex formation between ceric ions and sulphate ions in aqueous solution. Jones and Soper (2) have measured transference in solutions of high sulphuric concentration and found migration of color to the anode. Electromotive force measurements by Kunz (3), Noyes and Garner (6), Smith and Getz (7) indicate that a complex is certainly formed, but its nature could not be explicitly determined. Moore and Anderson (4) found evidence for complexing from kinetic studies on the reaction of ceric ions with arsenite ions. Smith and Getz infer the existence of ceric sulphate complexes from the formation of double salts such as $(\text{NH}_4)_2\text{Ce}(\text{SO}_4)_3$.

Moore and Anderson (5) made a spectral study on the first complex of ceric ion and sulphate in perchloric acid solutions. They analyzed their data by the limiting logarithmic method and the method of continuous variations. They determined the instability constant of the first complex and found it to vary with total ceric ion plus sulphate concentration. Evidence for higher complexes was obtained.

In view of the lack of accurate information on the complexes formed, it seemed advisable to investigate the ceric ion - sulphate ion system thoroughly. The most promising method appeared to be a spectral study supplemented by qualitative migration experiments.

Experimental

Materials

Ceric perchlorate solutions: These were prepared by the method described in the previous paper (1). The solutions contained no detectable chloride, sulphate, or nitrate.

Perchloric acid solutions were prepared from Merck's 70% perchloric acid. Sodium hydroxide solutions (carbonate-free) were prepared from Nichol's Reagent grade sodium hydroxide. Sodium sulphate solutions were prepared gravimetrically from Baker and Adams Reagent grade sodium sulphate. Test

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solutions were made by mixing appropriate amounts of these solutions to give the desired ceric ion concentration, sulphate concentration, acidity, and ionic strength.

Optical measurements were made using a Beckmann Quartz Photoelectric Spectrophotometer. The temperature of the test solutions was kept at $25.0 \pm 1^\circ\text{C}$. The procedure in making measurements was identical with that outlined in the previous paper (1).

In order to characterize the system ceric ion - sulphate ion, the various complexes present must be known, together with their extinction coefficients for particular wave lengths and the association constants which relate the various complexes.

It has been indicated that the complex $\text{Ce}(\text{SO}_4)_3^-$ is present in high sulphate concentrations. As will be shown later, the sulphate complexes contain no hydrogen, or hydroxyl ion; hence it will be assumed that the species Ce^{4+} (unassociated), CeSO_4^{++} , $\text{Ce}(\text{SO}_4)_2$, and $\text{Ce}(\text{SO}_4)_3^-$ are present under the proper conditions.

In a previous paper it was shown that in perchloric acid solutions, ceric ion is most probably present as a mixture of Ce^{4+} , CeOH^{3+} , and $(\text{Ce-O-Ce})^{6+}$. The association constants relating these ions have been determined, together with the molar extinction coefficients of each ion. Thus the relative amounts of the ions, and the optical density of the solution can be determined for any ceric ion concentration in perchloric acid solution. In the remainder of this report Ce^{4+} will be taken to mean ceric ion unassociated with sulphate, regardless of its state of hydrolysis or dimerization. The term ϵ_0 , the extinction coefficient of unassociated ceric ion, will be defined by

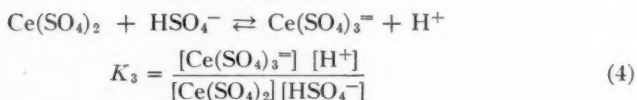
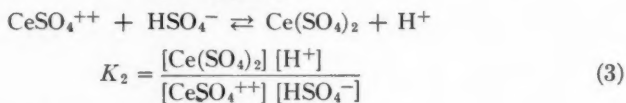
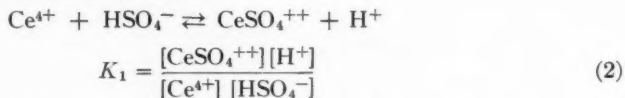
$$\epsilon_0 = \frac{\epsilon_{\text{Ce}^{4+}} C_{\text{Ce}^{4+}} + \epsilon_{\text{CeOH}^{3+}} C_{\text{CeOH}^{3+}} + \epsilon_{(\text{Ce-O-Ce})^{6+}} C_{(\text{Ce-O-Ce})^{6+}}}{C_{\text{Ce}^{4+}} + C_{\text{CeOH}^{3+}} + 2 C_{(\text{Ce-O-Ce})^{6+}}} \quad (1)$$

A small amount of cerous ion was invariably present in all samples, arising from incomplete oxidation of stock cerium solution and/or reduction of ceric ion during dilution. However, under the conditions used in these experiments, cerous ion does not absorb light. There is a possibility that sulphate concentration might be significantly reduced by the formation of a cerous-sulphate complex, but this has been neglected as no correction to equilibrium sulphate concentration from this source seems indicated in the calculation of association constants.

It was not certain whether the ceric sulphate complexes contained hydrogen ion or hydroxyl ion. This was resolved by determining the optical density of ceric ion solutions which had a fixed hydrogen ion to bisulphate ion ratio over a range of acid concentrations. Under these conditions, as bisulphate ion is a weak acid, the sulphate ion concentration remains constant but the bisulphate ion concentration varies. A change in optical density indicates either a change in the relative concentrations of the complexes, i.e. that bisulphate ion entered

the complex as a unit or that hydroxyl ion is present in the complex. It was found experimentally that negligible change occurred; hence it was concluded that associated ceric sulphate does not contain hydrogen or hydroxyl ions.

The data obtained are required to establish the thermodynamic constants of the following association equilibria:



For convenience, the following symbols have been adopted:

C_0 , C_1 , C_2 , and C_3 are the equilibrium concentrations of Ce^{4+} , CeSO_4^{++} , $\text{Ce}(\text{SO}_4)_2$, and $\text{Ce}(\text{SO}_4)_3^=$ respectively and ϵ_0 , ϵ_1 , ϵ_2 , and ϵ_3 are the corresponding molar extinction coefficients. At a particular wave length, the subscript of the wave length in millimicrons will be used, e.g. $\epsilon_{1.395}$.

C_T is the total concentration of tetravalent cerium in solution.

S and S_T are the equilibrium and total concentrations of HSO_4^- respectively in solution. At concentrations above 0.1 M HSO_4^- the difference in values between these two quantities is negligible under the conditions of this study.

The equilibrium equations now become

$$K_1 = \frac{C_1[\text{H}^+]}{C_0 S} \quad (2a)$$

$$K_2 = \frac{C_2[\text{H}^+]}{C_1 S} \quad (3a)$$

$$K_3 = \frac{C_3[\text{H}^+]}{C_2 S} \quad (4a)$$

First Complex $\text{Ce}(\text{SO}_4)^{++}$

A series of solutions was made up in which the total sulphate concentration was maintained at $1.00 \times 10^{-3} M$ and the total ceric ion concentration varied from 0.16×10^{-3} to $5.2 \times 10^{-3} M$. The molar ionic strength Γ was 2.00, and the acidity 1.00 N in all cases. The optical density of these solutions was measured from 395 $m\mu$ to 430 $m\mu$ in steps of 5 $m\mu$. The optical density of the solutions at 400 $m\mu$ is plotted against total ceric ion concentration in Fig. 1.

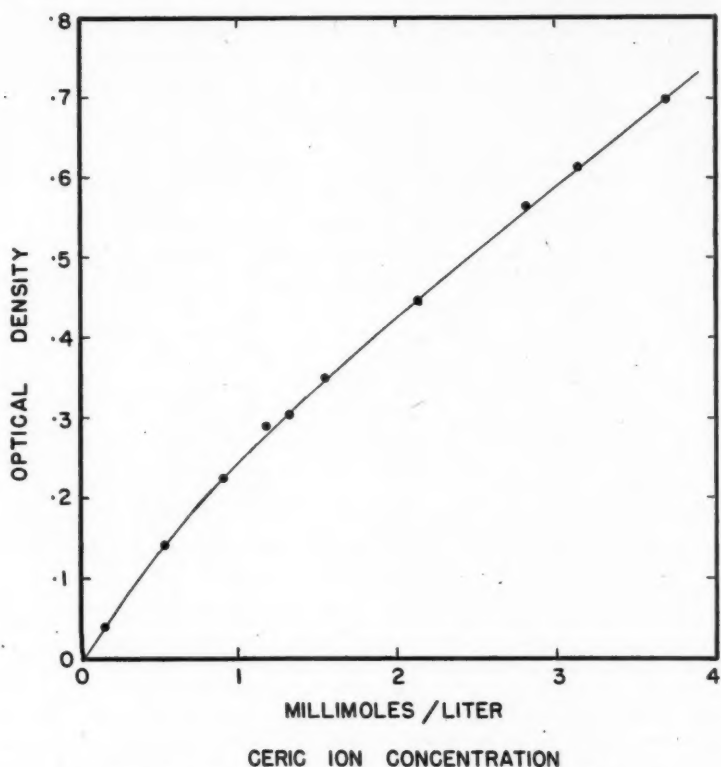


FIG. 1. Optical density as a function of ceric ion concentration. Total sulphate concentration = 1.00×10^{-2} moles/liter. $[H^+] = 1.00$ N. $\lambda = 400$ m μ .

From Equation (2a)

$$K_1 = \frac{C_1[H^+]}{(C_T - C_1)(S_T - C_1)} \quad (2b)$$

$$C_1 = \frac{1}{2} \left[\left\{ C_T + S_T + \frac{[H^+]}{K_1} \right\} - \sqrt{\left(C_T + S_T + \frac{[H^+]}{K_1} \right)^2 - 4C_T S_T} \right] \quad (5)$$

$$D = \sum \epsilon_i C_i$$

$$= \epsilon_0 C_T + \frac{1}{2} (\epsilon_1 - \epsilon_0) \left[\left\{ C_T + S_T + \frac{[H^+]}{K_1} \right\} - \sqrt{\left(C_T + S_T + \frac{[H^+]}{K_1} \right)^2 - 4C_T S_T} \right] \quad (6)$$

Direct solution of this equation is not simple. However, by successive approximations values of K_1 and ϵ_1 are obtained which will fit the curve in Fig. 1. This value of K_1 is used to find ϵ_1 values at other wave lengths. Optical den-

sities calculated from these ϵ_1 values fitted the curves well throughout the whole range of ceric ion concentrations, which demonstrates that K_1 was reasonably well chosen. The values of ϵ_1 are recorded in Table I. The value of K_1 obtained was 3500.

TABLE I
MOLAR EXTINCTION COEFFICIENTS

Wave length m μ	ϵ_0^*	$\epsilon_{\text{CeSO}_4^{++}}$	$\epsilon_{\text{Ce}(\text{SO}_4)_2}$	$\epsilon_{\text{Ce}(\text{SO}_4)_3^-}$
430	56	109	246	286
425	67	138	296	358
420	79.3	160	351	441
415	93.5	192	426	546
410	110	228	506	666
405	130	270	608	812
400	153	320	730	982
395	176	383	890	1190

* Taken from $\bar{\epsilon}$ values for ceric perchlorate solutions at $10^{-3}M$ Ce^{IV} . This includes Ce^{4+} , CeOH^{3+} , and $(\text{Ce}-\text{O}-\text{Ce})^{4+}$ as reported in the previous paper (1).

In order to check these values, solutions containing sulphate ion ($5 \times 10^{-4}M$) and excess ceric ion were made up. The measured optical densities were compared with those calculated from the molar extinction coefficients in Table I. The agreement was within 0.6%.

The Higher Complexes $\text{Ce}(\text{SO}_4)_2$ and $\text{Ce}(\text{SO}_4)_3^-$

The extinction coefficients of the highest complex ϵ_3 , may be found by measuring the light absorption of solutions which are low in ceric ion and high in sulphate ion. A series of solutions where $C_T = 1.00 \times 10^{-3}M$, $[\text{H}^+] = 1.00M$, $\Gamma = 2.00$, and sulphate concentration varied from 0.12 to 0.7 M , were tested in this manner. A plot of optical density against total sulphate ion (Fig. 2) shows that the optical density approaches an asymptote, the value of which is $\epsilon_3 C_T$. The ϵ_3 values are recorded in Table I.

The values for ϵ_2 and K_2 may be determined by assuming that from about 0.12 M sulphate to 0.7 M sulphate the only complexes present are $\text{Ce}(\text{SO}_4)_2$ and $\text{Ce}(\text{SO}_4)_3^-$. Deviations of the optical density from the value $\epsilon_3 C$ indicate the presence of the second complex. In this region one can assume that $S \cong S_T$. From Equation (4a)

$$K_3 = \frac{C_3[\text{H}^+]}{(C_T - C_3)S} \quad (7)$$

$$C_3 = \frac{K_3 C_T S}{[\text{H}^+] + K_3 S} \quad (8)$$

$$C_2 = C_T - C_3 = \frac{[\text{H}^+] C_T}{[\text{H}^+] + K_3 S} \quad (9)$$

$$\begin{aligned} D &= \epsilon_2 C_2 + \epsilon_3 C_3 \\ &= \epsilon_3 C_T - \frac{[\text{H}^+] C_T (\epsilon_3 - \epsilon_2)}{[\text{H}^+] + K_3 S} \end{aligned} \quad (10)$$

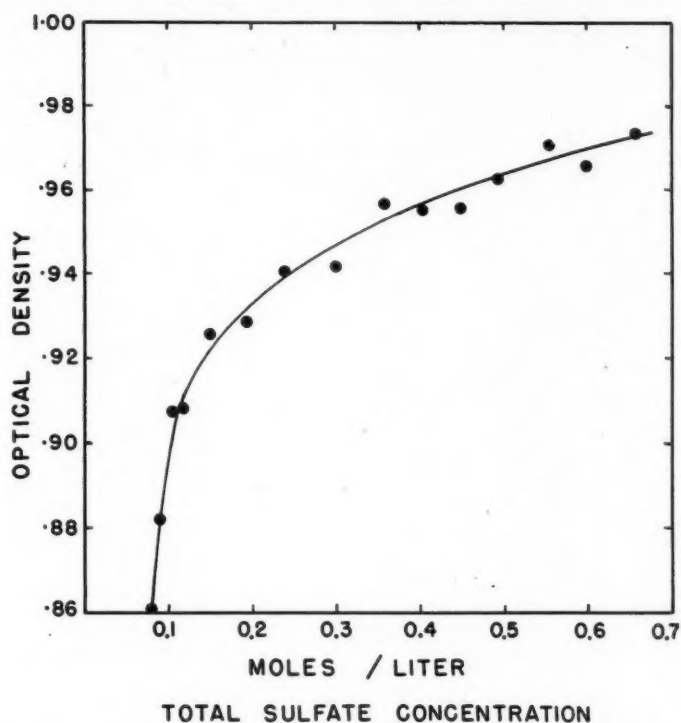


FIG. 2. Optical density as a function of sulphate ion concentration. Total ceric ion concentration = 1.00×10^{-3} moles/liter. $[H^+] = 1.00$ N. $\lambda = 400$ m μ .

By successive approximations, values of K_3 and ϵ_2 may be found which will satisfy Equation (10). The value of K_3 is 20; ϵ_2 values are recorded in Table I.

To determine K_2 , the optical densities of solutions of the following composition were measured: $C_T = 1.00 \times 10^{-3}$ M $[H^+] = 1.00$ M $\Gamma = 2.00$, and total sulphate was varied from .004 M to 0.12 M. The results are plotted in Fig. 3.

From equation

$$\frac{C_3}{C_2} = \frac{K_3 S}{[H^+]} \quad (4b)$$

and
$$\frac{C_2}{C_1} = \frac{K_2 S}{[H^+]} \quad (3b)$$

one obtains
$$\frac{C_3}{C_1} = \frac{K_2 K_3 S^2}{[H^+]^2} \quad (11)$$

Substituting in $C_T = C_1 + C_2 + C_3$

one obtains

$$C_T = C_1 \left(1 + \frac{K_2 S}{[H^+]} + \frac{K_2 K_3 S^2}{[H^+]^2} \right) \quad (12)$$

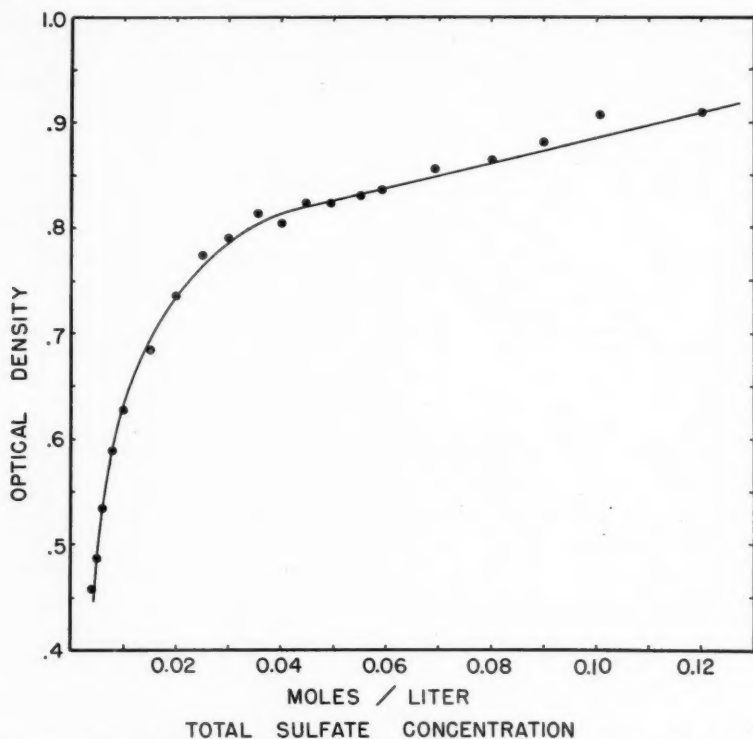


FIG. 3. Optical density as a function of sulphate ion concentration. Total ceric ion concentration = 1.00×10^{-3} moles/liter. $[H^+] = 1.00$ N. $\lambda = 400$ m μ .

If a value of K_2 is assumed, then one can calculate C_1 , C_2 , and C_3 , and hence the optical density of the solution. A comparison with the measured optical density indicates the accuracy of the K_2 value chosen. By successive approximation one can obtain a value of K_2 which will give good agreement between measured and calculated optical densities. The value of K_2 determined in this way was 200.

At the sulphate concentrations used for the evaluation of K_2 , the amount of sulphate associated with the ceric ion is an appreciable fraction of the total. In Fig. 3 the total sulphate is plotted against optical density. To find the correct optical density, an approximate value of K_2 must be known in order to determine the equilibrium concentration of sulphate. This correction, however, is simply applied as part of the method of successive approximations.

The association constants were calculated from data obtained at 400 and 395 m μ . Fig. 4 shows a comparison of the measured with calculated optical densities as a function of total sulphate concentration. The agreement is good over the whole range. The values of the association constants and extinction coefficients are therefore quite satisfactory.

In Fig. 5 the fraction of the cerium in each stage of association is plotted as a function of total sulphate concentration. It is not possible to obtain one type of association complex free from the others, except at high sulphate concentrations.

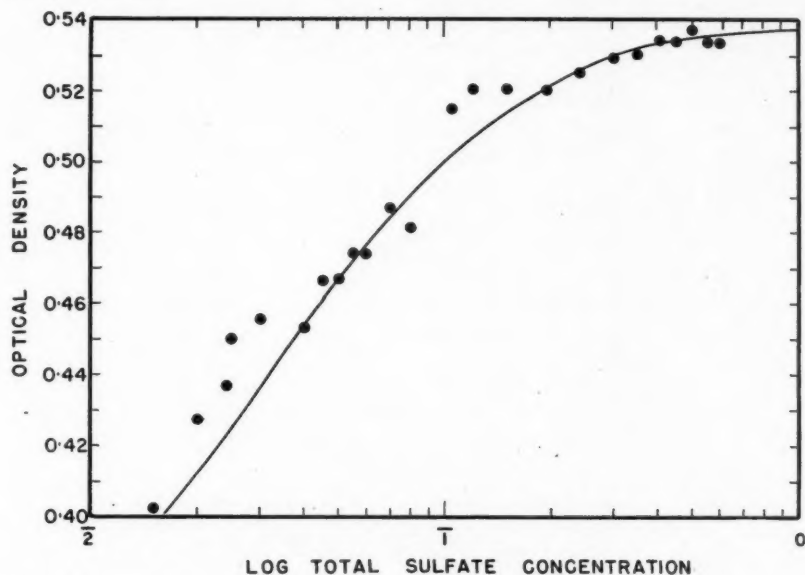


FIG. 4. Comparison of calculated and measured optical density as a function of total sulphate concentration. Total ceric ion concentration = 1.00×10^{-3} moles/liter. $[H^+] = 1.00 N$. $\lambda = 415$ m μ . Straight line represents calculated values; circles, experimental points.

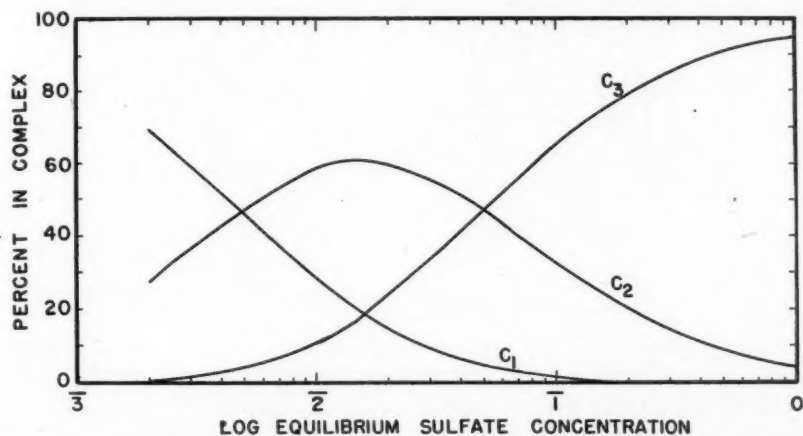


FIG. 5. Per cent of ceric ion present in each complex as a function of sulphate concentration. Total ceric ion concentration = 1.00×10^{-3} moles/liter.

Migration Experiments

Qualitative migration experiments were made in order to obtain the charge on the ions at various sulphate concentrations. A three compartment cell with fine sintered glass partitions was used (Fig. 6). In the center compartment a ceric solution was placed $[H^+] = 1.00M$, $\Gamma = 2.00$, $[Ce^{IV}] = 1.00 \times 10^{-3}M$ and containing various amounts of sulphate. In the outer compartments an identical solution was placed, but containing no ceric ion. All liquid levels were equal. Migration was determined by the appearance of color in the outer compartments. A potential of 67 1/2 volts was applied at electrodes placed in the outer cells. The results are found in Table II.

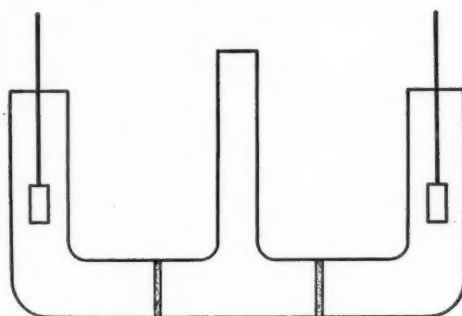


FIG. 6. Three compartment migration cell.

TABLE II
RESULTS OF MIGRATION EXPERIMENTS

All solutions $[H^+] = 1.00M$, $\Gamma = 2.00$;			$[Ce^{IV}] = 1.00 \times 10^{-3}M$ (center compartment only)
Soln.	Total conc. of sulphate moles/liter	Natural migration 24 hr.	Induced migration of color, direction
A	.01	None	Mostly towards cathode, small trace towards anode
B	.05	None	Migration both directions
C	.5	None	Towards anode only

These migration experiments are in complete agreement with the spectral results as recorded in Fig. 5. Solution A contains mostly $Ce(SO_4)^{++}$ and $Ce(SO_4)_2$ but with a small amount of $Ce(SO_4)_3^-$. Solution B contains similar amounts of all three forms. Solution C contains mostly $Ce(SO_4)_3^-$, a little $Ce(SO_4)_2$, but practically no $Ce(SO_4)^{++}$.

Discussion

It has been shown that ceric ion associates successively with one, two, and three sulphate ions to form complexes. As might be expected, the tendency to associate becomes smaller as the number of sulphate ions in the complex increases. There is no indication that more than three sulphates are ever associated with a ceric ion.

In concentrated ceric sulphate solution, practically all the cerium will be present as $\text{Ce}(\text{SO}_4)_3$. This corresponds to the tendency for ceric ion to form double sulphate salts such as ammonium ceric sulphate $(\text{NH}_4)_2\text{Ce}(\text{SO}_4)_3$.

The data presented in this paper do not agree with that reported by Moore and Anderson (5). We can offer no explanation for this. However, it can be pointed out that those workers used limiting logarithmic and continuous variations methods of analyzing their data, which we find cannot be used with our data, as the associated species overlap one another to such an extent. Furthermore, Moore and Anderson found that solutions of ceric perchlorate obeyed Beer's Law up to 0.01 *M*, whereas the deviations from Beer's Law formed the basis of a complete study in a previous paper (1). It is therefore difficult to reconcile the results from the two studies.

References

1. HARDWICK, T. J. and ROBERTSON, E. *Can. J. Chem.* 29: 818. 1951.
2. JONES, E. M. and SOPER, F. M. *J. Chem. Soc.* 802. 1935.
3. KUNZ, A. H. *J. Am. Chem. Soc.* 53: 98. 1931.
4. MOORE, R. L. and ANDERSON, R. C. *J. Am. Chem. Soc.* 66: 1476. 1944.
5. MOORE, R. L. and ANDERSON, R. C. *J. Am. Chem. Soc.* 67: 167. 1945.
6. NOYES, A. A. and GARNER, J. *J. Am. Chem. Soc.* 58: 1265. 1936.
7. SMITH, F. J. and GETZ, C. A. *Ind. Eng. Chem., Anal. Ed.* 10: 191. 1938.

THE PREPARATION OF ANHYDROUS SODIUM STEARATE¹BY G. STAINSBY,² R. FARNAND, AND I. E. PUDDINGTON

Abstract

A method for preparing sodium stearate by the action of sodium amalgam with stearic acid under moisture free conditions is described. From the similar density-temperature behavior of these samples and those prepared by titration of stearic acid followed by melting *in vacuo*, it is concluded that melting under low pressure completely removes the water associated with the sodium ion in soaps.

Previous publications have described dilatometric studies on anhydrous sodium soaps from room temperature to the isotropic liquid state (1, 2, 4, 5). Since these soaps apparently do not melt suddenly but pass through several phases before liquefaction, the studies are of considerable interest. However, the published results have been justifiably criticized on the grounds that the soaps used were not unambiguously anhydrous (3). In most cases the samples were prepared by titration followed by melting *in vacuo* (about 300°C.) to remove the water. It has been considered by Ralston that this treatment is not sufficiently drastic to remove the last traces of water associated with the sodium ion and the same opinion is expressed by Lawrence (2). In view of this it is implied that the peculiar dilatometric behavior of these compounds may be partially due to incomplete dehydration of the samples. The present communication describes a method of preparation which appears to overcome this objection and dilatometric measurements have been made on samples prepared by both methods.

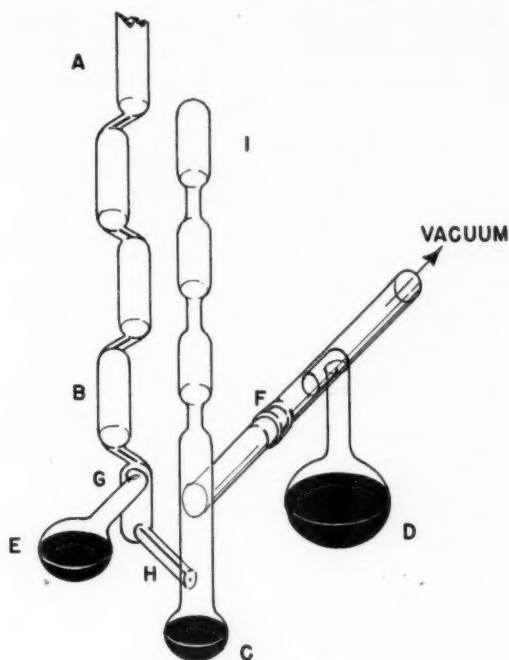
The soap was prepared by the action of sodium on stearic acid in a moisture free atmosphere. The apparatus is shown in Fig. 1 and the preparation was carried out as follows: Prior to assembly, a weighed quantity (5 gm.) of Eastman's white label stearic acid was placed in Flask C (capacity 10 cc.) and mercury in Flasks E and D (capacity 25 and 50 cc. respectively). Clean sodium in large excess of the amount required to neutralize the fatty acid was then placed in A. Tube A was immediately sealed off above the sodium and the pressure inside the apparatus reduced to 10^{-6} mm. The stearic acid was melted and boiled, the sodium melted, the mercury in Flasks E and D boiled, and the remainder of the apparatus strongly flamed.

The sodium was then freed from oxide. This was accomplished by filtering it through the 0.5 mm. capillaries in the column between A and B. Since the assembly could rotate freely about the ground glass joint at F, it was easy to control the flow of the molten sodium from bulb to bulb. Each bulb was sealed off as the sodium passed into the succeeding one. Bulb B was suffi-

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² Present address: British Glue and Gelatine Research Association, London, England.

FIG. 1. *Apparatus.*

ciently large to hold about 50% more sodium than required for the neutralization of the acid and it was used as a meter, the excess being sealed off in the previous bulb. Early experiments demonstrated that pure sodium was not suitable for neutralizing the acid. The reaction tended to be too vigorous initially and sodium became trapped in the soap. Further, if the mix were heated too strongly the fatty acid decomposed with considerable blackening. This occurred at temperatures in the vicinity of 300°C.

In order to modify the rate of reaction the sodium was amalgamated in G by distillation in an appropriate volume of mercury from E. The amalgam was then transferred to C and the capillary sealed off at H. Preliminary experiments showed that a good deal of foaming occurred if the reaction were allowed to proceed under the low pressure and to prevent this, an inert gas, dried by passage through a liquid nitrogen trap, was added until the pressure was approximately atmospheric. It has been demonstrated frequently that sodium does not readily react with some acids when the system is completely anhydrous. The reaction between sodium and stearic acid proceeded smoothly under the conditions described above, however, and the temperature was gradually increased, by placing an air bath about Bulb C, until a temperature of about 300°C. was reached and no further hydrogen was evolved. The pressure in the system was then reduced to a hard vacuum and cooled until

the soap solidified and pulled away from the walls. By rotating the apparatus through 180° and gently tapping it, virtually all of the residual amalgam flowed into I. This bulb was then sealed off and the assembly again rotated through 180° for further washing with fresh mercury.

In some cases if the amalgam were allowed to cool for an extended period either in G or C it formed a solid that was quite difficult to remelt. No difficulty was encountered when the procedure was carried out continuously. Any residue of the amalgam was removed by washing the soap twice with mercury. The mercury was distilled in from D, the inert gas added, and the soap melted as before, followed by the cooling and decanting of the mercury washings into the bulbs below I.

The soap was finally melted and degassed under a hard vacuum. After cooling, mercury was distilled into Flask C until the neck was partially filled. The neck was constricted and cut off, after air was admitted to the system. The remainder of the dilatometer was then sealed on, evacuated, and completely filled with mercury.

Some experiments that were of considerable interest were carried out to obtain information on the thermal stability of the sodium stearate. Soap containing free fatty acid produced water and stearone when highly heated, until the excess acidity was removed. This reaction is easily detected when carried out at low pressure as the water and ketone deposit in separate bands on the cool part of the apparatus. The neutral soap appears to be very stable and, if oxygen is excluded, may be heated for at least 16 hr. at 350°C . with no apparent decomposition. The above decomposition was first noted when an attempt was made to prepare soap with insufficient sodium. No difficulty was encountered when an excess of sodium was used and the reaction kept at 200° – 250°C . until substantially complete.

After completing the dilatometric measurements the soap samples were removed, weighed, and analyzed. The results are shown in Table I. The sample prepared using insufficient sodium to react with the stearic acid was neutral but was low in ash and also low in stearic acid when titrated with standard hydrochloric acid. The samples prepared using excess sodium, however, showed no significant departure from the theoretical. These samples were white solids and melted to give liquids with a faint yellow color.

TABLE I
ANALYSIS OF SODIUM STEARATE SAMPLES

Sample	Sodium used	% Ash	M.p. recovered stearic acid	Free acidity or alkalinity
1	Insufficient	15.4	—	Neutral
2	Excess	17.3	68.6	Neutral
4	Excess	17.2	—	Neutral
Theoretical	—	17.3	68.8	

The volume changes were determined using a weight dilatometer and an air thermostat that could be controlled to better than $\pm 0.05^\circ\text{C}$. over the range 25° to 350°C . Calibrated complete immersion thermometers were used to avoid stem corrections. Some difficulty was experienced in obtaining reproducibility in the weight of mercury expelled by the dilatometers at temperatures below 130°C . when the samples were taken to about 300° and then cooled. This seemed to be due to cavitation within the sample, on cooling. To reduce this effect the arms of the dilatometers were extended with 0.5 mm. capillary to give a pressure of about 4 atm. on the samples. Using this device, it was possible to go through the cycle of melting to isotropic liquid and cooling to room temperature several times with no substantial change in the low temperature volume.

For comparison, the density-temperature relations of a sample of sodium stearate prepared by neutralizing an alcoholic solution of stearic acid with alcoholic sodium hydroxide were determined concurrently. The behavior of the samples is shown in Fig. 2, where the weight of mercury (in grams) expelled from the dilatometers is plotted as a function of temperature. Samples 2 and 4 were prepared as described above. Sample 3 was obtained by neutralizing the stearic acid with alcoholic sodium hydroxide. As the same sample weights

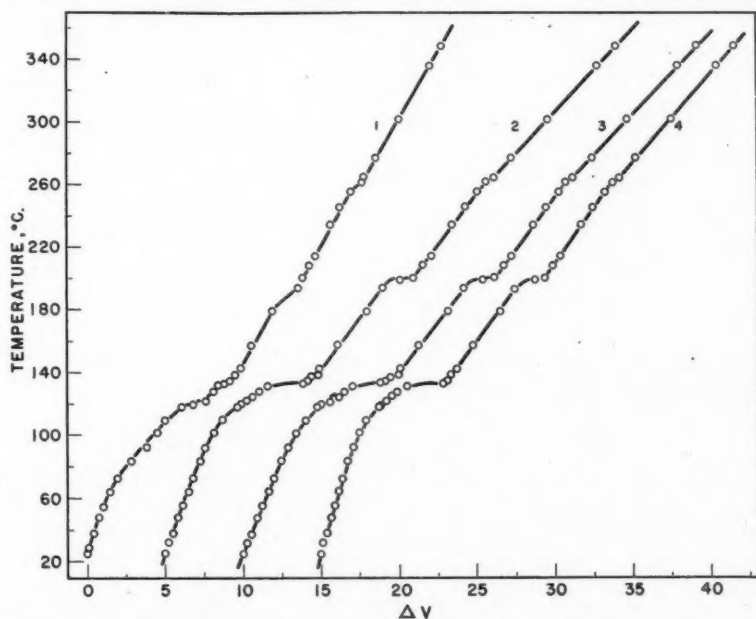


FIG. 2. Dilatometric behavior of anhydrous sodium stearate. Graphs from left to right represent respectively the behavior of samples prepared (1) from sodium and stearic acid using an excess of stearic acid, (2) from sodium and stearic acid using an excess of sodium, (3) from sodium hydroxide and stearic acid by titration, and (4) from sodium and stearic acid using an excess of sodium.

and similar dilatometers were used, the slopes should be comparable. Sample 1 indicates the behavior when insufficient sodium was used in the preparation. The sample weight here is also less than with the other preparations, which accounts for the difference in slope. It would seem probable that the extra points of discontinuity that occur in the graph representing the behavior of this sample are due to the presence of the decomposition products of the excess fatty acid that it contains.

Since the dilatometric behavior of the other three samples appears to be identical, it would seem that melting the soap under low pressure is sufficient to render it anhydrous.

References

1. GALLAY, W. and PUDDINGTON, I. E. *Can. J. Research, B*, 21: 202. 1943.
2. LAWRENCE, A. S. C. *Trans. Faraday Soc.* 34: 660. 1938.
3. RALSTON, H. W. *Fatty acids and their derivatives*. John Wiley & Sons Inc., New York. 1948. p. 889.
4. SOUTHAM, F. W. and PUDDINGTON, I. E. *Can. J. Research, B*, 25: 121. 1947.
5. VOLD, M. J., MACOMBER, M., and VOLD, R. D. *J. Am. Chem. Soc.* 63: 168. 1941.

SYNTHESIS AND ULTRAVIOLET ABSORPTION OF SOME PYRAZOLONES¹

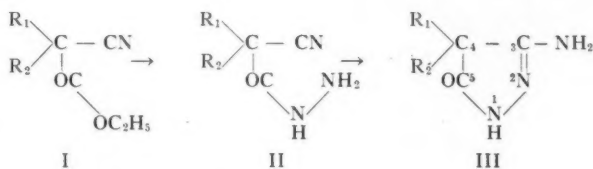
BY P. E. GAGNON, B. NOLIN,² AND R. N. JONES

Abstract

Thirteen 3-amino-5-pyrazolones substituted only in position 4 have been synthesized from the corresponding mono- or disubstituted cyanoacethydrazides or cyanoacetic esters in alkaline medium. Their ultraviolet light absorption spectra have been determined in neutral and acid solutions.

Introduction

In 1947, the preparation of 3-amino-5-pyrazolones substituted only in position 4 was reported for the first time (6). The authors prepared substituted cyanoacetic esters (I) and found that the corresponding crude acethydrazides (II) could undergo transformation into 4-substituted-3-amino-5-pyrazolones (III).



R₁, R₂ = H, alkyl or aryl group

This reaction was recently reinvestigated (1, 2, 3, 4).

In the present work, eight 4-monosubstituted and five 4,4-disubstituted-3-amino-5-pyrazolones were synthesized and their ultraviolet absorption spectra determined.

Experimental

Pyrazolones of both types were soluble in water, acids, and alkalies, and insoluble in ether and sodium bicarbonate solution. The 4 monosubstituted compounds, however, were more soluble in water than the 4,4-disubstituted ones.

They all gave a positive color test with ferric chloride, which is indicative of the presence of an actual or potential hydroxyl group. The nitrous acid test was also positive, indicating the presence of an amino group.

The individual properties are summarized in Table I. Melting points are uncorrected.

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² Holder of a Studentship under the National Research Council of Canada (1948-49). Present address: National Research Council, Ottawa, Canada.

4-Monosubstituted-3-amino-5-pyrazolones

With the exception of 4-acethydrazide-3-amino-5-pyrazolone, these compounds were prepared by treatment of the corresponding hydrazides (5) with strong alkalis as described in (3).

4-Acethydrazide-3-amino-5-pyrazolone was obtained directly from α -cyano-diethyl succinic ester and hydrazine hydrate. When two equivalents of hydrazine were slowly added to the ester, dissolved in cold ethanol or not, the intermediate dihydrazide could not be isolated but was cyclized into the corresponding pyrazolone.

4, 4-Disubstituted-3-amino-5-pyrazolones

These compounds were prepared by heating disubstituted cyanoacetic esters with hydrazine hydrate in the presence of sodium ethylate. The detailed preparation was reported previously (3).

4,4-Diethyl-3-amino-5-pyrazolone was also obtained by mixing the corresponding ester with hydrazine hydrate at room temperature. The melting points of the sample prepared in both ways were the same and a mixed melting point was not depressed.

The other disubstituted pyrazolones could not be obtained in the latter way.

Ultraviolet Absorption Spectra

The ultraviolet absorption spectra were determined on a Beckman spectrophotometer Model DU in neutral (95% ethanol) and acid (*N*/10 aqueous hydrochloric acid in 95% ethanol) solutions. The experimental details have been reported previously (6).

TABLE I
PROPERTIES OF INDIVIDUAL PYRAZOLONES

Compound	Formula	M.p., °C.	Analysis		Absorption maxima			
			Nitrogen, %		Neutral solvent		Acid solvent	
			Calc.	Found	Wave length, Å.	Intensity, log E_m	Wave length, Å.	Intensity, log E_m
4-Monosubstituted-3-amino-5-pyrazolones								
4- <i>n</i> -Hexyl-	C ₉ H ₁₇ ON ₂	133-135	22.9	22.8	2880	3.58	2820	3.60
4- <i>n</i> -Heptyl-	C ₁₀ H ₁₉ ON ₂	136-138	21.3	21.0	2870	3.58	2810	3.60
4- <i>n</i> -Decyl-	C ₁₃ H ₂₅ ON ₂	234-235	17.6	17.9	2840	3.59	2770	3.61
4-(2-Ethyl- <i>n</i> -butyl)-	C ₁₀ H ₁₉ ON ₂	190-196	22.9	22.8	2880	3.56	2820	3.57
4-(2-Ethyl- <i>n</i> -hexyl)-	C ₁₃ H ₂₅ ON ₂	131-132	19.9	20.2	2890	3.54	2820	3.57
4-Cyclohexyl-	C ₈ H ₁₅ ON ₂	239-241	23.2	23.3	2870	3.57	2820	3.58
4-(α -Naphthylmethyl)-	C ₁₄ H ₁₅ ON ₂	Dec.	17.6	17.8	2950	3.89	2950	3.85*
					2830	4.00	2830	3.99
					2730	3.92	2730	3.92
					2240	4.91	2240	4.89
4-Acethydrazide-	C ₆ H ₉ O ₂ N ₃	212-213	40.9	41.0	2410	4.16	2320	4.05
4, 4-Disubstituted-3-amino-5-pyrazolones								
4, 4-Dimethyl	C ₆ H ₉ ON ₂	249-251	33.0	33.2	2690	3.69	2610	3.74
4, 4-Diethyl	C ₇ H ₁₁ ON ₂	208-209	27.1	27.2	2710	3.67	2630	3.75
4, 4-Di- <i>n</i> -propyl-	C ₉ H ₁₇ ON ₂	236-239	22.9	22.9	2710	3.69	2640	3.71
4, 4-Di- <i>n</i> -butyl-	C ₁₁ H ₂₁ ON ₂	223-225	19.9	20.1	2710	3.67	2630	3.71
4, 4-Di- <i>n</i> -amyl-	C ₁₃ H ₂₅ ON ₂	200-201	17.6	17.7	2710	3.66	2630	3.66

* Inflection point.

The intensities of the absorption maxima are listed in Table I and representative spectra are plotted in Figs. 1-4.

4-Monosubstituted-3-amino-5-pyrazolones

The spectrum of 4-*n*-hexyl-3-amino-5-pyrazolone (Fig. 1) is representative of those given by the compounds containing alkyl or cyclohexyl substituents at position 4.

The spectrum of 4-(α -naphthylmethyl)-3-amino-5-pyrazolone is dominated by the absorption of the naphthalene chromophore. This is illustrated in Fig. 2

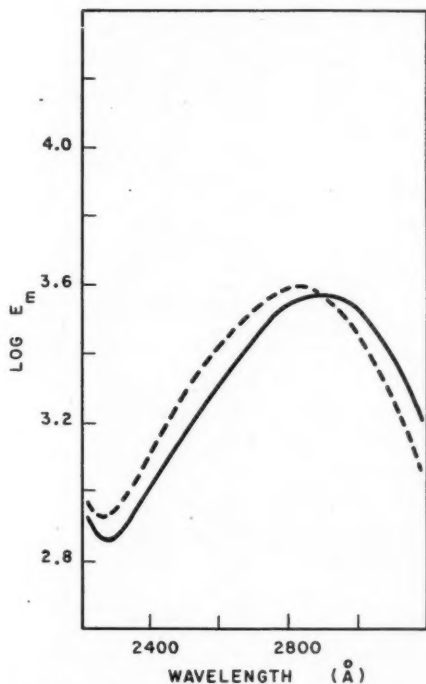


FIG. 1. Ultraviolet absorption spectra.
— 4-*n*-Hexyl-3-amino-5-pyrazolone (neutral).
--- 4-*n*-Hexyl-3-amino-5-pyrazolone (acid).

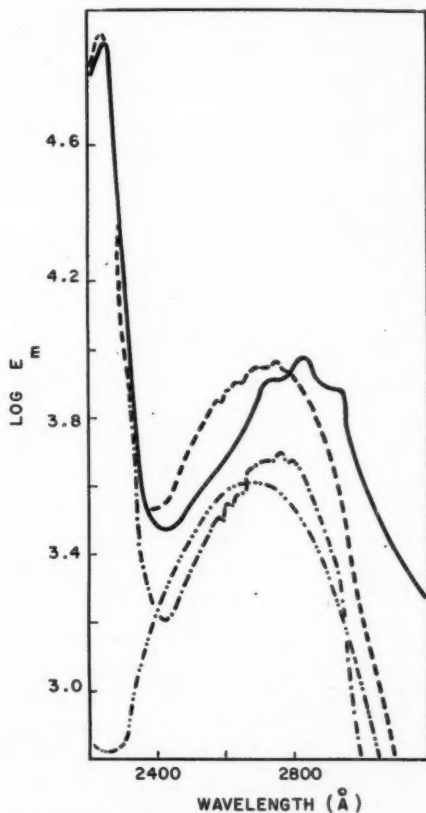


FIG. 2. Ultraviolet absorption spectra.
A --- α -Methylnaphthalene (neutral).
B 4-Methyl-3-amino-5-pyrazolone (neutral). Taken from Ref. 3.
C - - - Calculated curve obtained by addition of Curve A and Curve B.
D — 4-(α -Naphthylmethyl)-3-amino-5-pyrazolone (neutral).

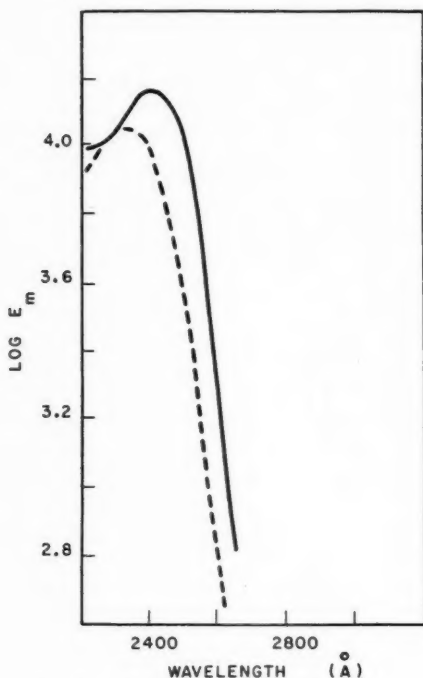


FIG. 3. Ultraviolet absorption spectra.
 — 4-Acethydrazide-3-amino-5-pyrazolone (neutral).
 --- 4-Acethydrazide-3-amino-5-pyrazolone (acid).

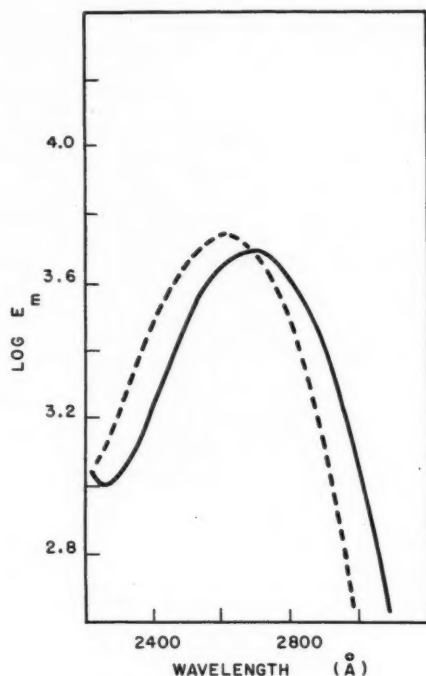


FIG. 4. Ultraviolet absorption spectra.
 — 4, 4-Dimethyl-3-amino-5-pyrazolone (neutral).
 --- 4, 4-Dimethyl-3-amino-5-pyrazolone (acid).

where its spectrum is compared with the curve resulting from the addition of the spectrum of α -methylnaphthalene and that of 4-methyl-3-amino-5-pyrazolone (3).

The 4-acethydrazide derivative (Fig. 3) shows an absorption maximum of high intensity at a shorter wave length than those observed for the compounds containing alkyl or cyclohexyl substituents.

4, 4-Disubstituted-3-amino-5-pyrazolones

The spectrum of 4,4-dimethyl-3-amino-5-pyrazolone (Fig. 4) is typical of the spectrometric behavior of all the 4,4-dialkyl derivatives.

Concluding Remarks

The similarity of the spectra of the 4-monoalkyl, 4-cyclohexyl, and 4, 4-dialkyl compounds supports their formulation in terms of the bond structure III in which the cyclic double bond is placed at the 2:3 position.

The only effect of the pyrazolone ring on the absorption of 4-(α -naphthylmethyl)-3-amino-5-pyrazolone is to shift the maxima of the naphthalene chromophore towards the visible. Since it cannot be in conjugation with the naphthyl group, its additive contribution to the total absorption of the molecule is negligible.

The spectrum of the 4-acethydrazide pyrazolone is different from those of 4-mono- or 4,4-dialkyl compounds. This is indicative of a difference in the pyrazolone ring since C-alkyl-substituted acethydrazides have been found not to absorb in the same spectral region. It is suggested that the cyclic double bond is at the 3:4 position.

References

1. GAGNON, P. E., BOIVIN, J. L., BOIVIN, P. A., and JONES, R. N. *Can. J. Chem.* 29: 182. 1951.
2. GAGNON, P. E., BOIVIN, J. L., and GIGUÈRE, J. *Can. J. Chem.* 29: 328. 1951.
3. GAGNON, P. E., BOIVIN, J. L., and JONES, R. N. *Can. J. Research, B*, 27: 190. 1949.
4. GAGNON, P. E., BOIVIN, J. L., and JONES, R. N. *Can. J. Research, B*, 28: 34. 1950.
5. GAGNON, P. E. and NOLIN, B. *Can. J. Research, B*, 27: 742. 1949.
6. GAGNON, P. E., SAVARD, K., GAUDRY, R., and RICHARDSON, E. D. *Can. J. Research, B*, 25: 28. 1947.

INFLUENCE OF SHEAR ON THE DIELECTRIC CONSTANT OF LIQUIDS¹

BY B. L. FUNT² AND S. G. MASON³

Abstract

The effects of a velocity gradient upon the dielectric constant were studied in solutions of macromolecules, in suspensions and in liquid crystals. Decreases in dielectric constant under shear were observed for polar polymers in polar and nonpolar solvents. For solutions of ethyl cellulose an increase in dielectric constant was obtained. Nonpolar polymers showed no changes of dielectric constant under shear. Large changes in dielectric constant at low rates of shear were observed in carbon black suspensions. The experimental results are discussed on the basis of particle orientation in a velocity gradient and in an electric field.

Introduction

The behavior of asymmetric molecules subjected to external electrical and mechanical forces is of considerable interest. If the molecules are geometrically asymmetric it is reasonable to predict that, in solution, they would become oriented when subjected to a sufficiently high rate of shear. The hydrodynamic principles governing this type of orientation have been extensively investigated for particles of idealized shape in dilute solutions (1). Furthermore, the phenomenon of non-Newtonian viscosity has been predicted from theoretical considerations for systems in which orientation in a velocity gradient occurs (1). A system is considered to be non-Newtonian when the apparent viscosity is a function of the rate of shear at which it is measured. Such behavior, particularly when manifested as thixotropy, is common in solutions of macromolecules and in colloidal systems (3).

An extremely convincing manifestation of the orientation of geometrically asymmetric particles when they are subjected to shear is indicated optically (2). A solution of long-chain cylindrically shaped molecules is normally isotropic. When such a system is subjected to a sufficiently high rate of shear it becomes optically anisotropic, and the phenomenon is termed streaming birefringence.

If, in addition to being geometrically asymmetric, a molecule is also electrically asymmetric, another type of orientation can occur. A molecule possessing a permanent dipole moment will tend to align itself when placed in an electric field. The extent of the electrical orientation can be determined by measurement of the dielectric constant of the material.

It was the purpose of this investigation to determine the interplay of these two possible types of orientation in suitable molecular systems. In particular,

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it was thought that, if these two types of orientation opposed one another, a decrease in dielectric constant might be found experimentally, whereas if the orientations were additive, an increase in dielectric constant would be found.

Although orientation cannot be considered the only factor responsible for non-Newtonian behavior, nor indeed for streaming birefringence, it was felt that measurements of the dielectric constant under shear could, in principle, yield useful information regarding these phenomena and the structure of molecular systems. Small but definite changes in some of the systems studied were noted, but for reasons discussed later the interpretation is difficult.

Apparatus

A General Radio type 716C Schering bridge was used for the electrical measurements. The bridge was fed by a Hewlett-Packard audio-frequency oscillator. The null point was determined on an oscilloscope fed from the bridge through an intermediate amplifier and phase shifting network. This arrangement permitted rapid, simultaneous balance of the resistive and capacitive components of the test condenser. A reproducibility of $.03 \mu\text{f.}$ in measuring $1000 \mu\text{f.}$ was obtainable.

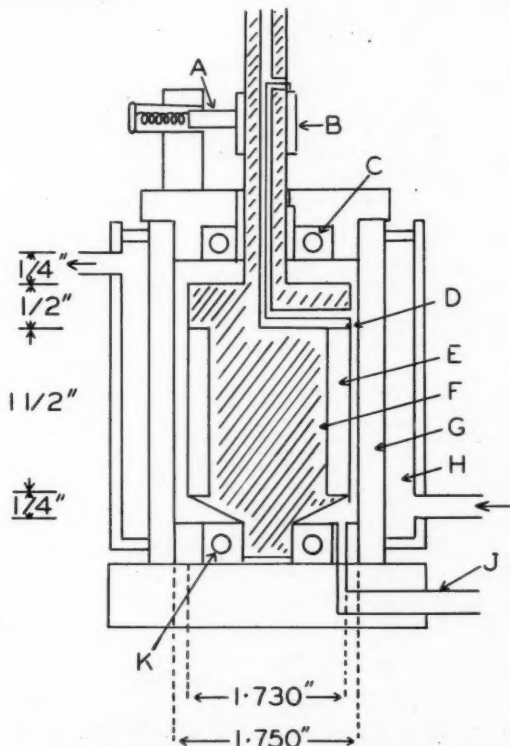


FIG. 1. Rotating cylindrical condenser.

The design of rotating condensers suitable for the proposed measurements presented difficulties. The dimensions and design had to fulfil, amongst others, the requirements of (1) absence of variation in capacitance of greater than 0.2% during rotation, (2) a suitable capacitance and shear gradient, and (3) absence of turbulent flow at the highest rates of shear employed.

Several rotating condensers were used in this work. All were of the coaxial cylindrical type with the inner cylinder rotating and were designed to avoid the possibility of drawing in air. One of the models used is shown in Fig. 1. Here A and B are the contact brush and contact ring; C, K are ball bearings; E is a brass sleeve on an insulating bakelite shaft, F, G indicates the outer brass cylinder, H the water jacket, and J the filling vent.

Results

Polymers in Nonpolar Solvents

Changes in dielectric constant were found when solutions of polar polymers in nonpolar solvents were subjected to shear.

In Fig. 2 are shown the changes in dielectric constant with shear for ethyl cellulose and polyvinyl acetate in benzene at 10 Kc. The polyvinyl acetate solutions were of two molecular weights commercially designated as Gelva V-15 and V-200. The percentage concentrations, expressed as gm. per 100 ml. of solvent, were 15% for the ethyl cellulose and Gelva V-200, and 30% for the Gelva V-15.

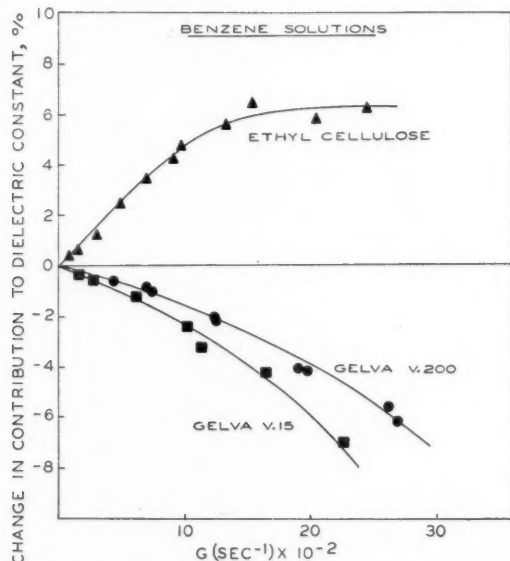


FIG. 2. Change of dielectric constant with rate of shear for solutions of ethyl cellulose and polyvinyl acetate. Measurements were carried out at 10 Kc.

The rate of shear, G , is expressed as $G = R \frac{d\omega}{dR}$ in units of reciprocal seconds. Here ω is the angular velocity of the liquid at the radial distance R .

The changes in dielectric constant are expressed as percentage changes by the relationship

$$\frac{\Delta\epsilon}{\epsilon_s - \epsilon_0} \times 100$$

where $\Delta\epsilon$ is the dielectric constant change under shear, ϵ_s is the rest value of the dielectric constant of the solution, and ϵ_0 is the dielectric constant of the pure solvent.

After rotation ceased, the dielectric constants returned to their original values, as shown in Fig. 3.

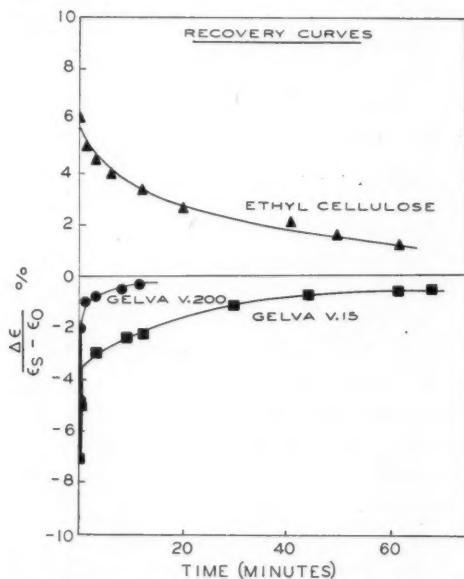


FIG. 3. Recovery of dielectric constant in quiescent solutions after shearing at 2500 sec.⁻¹.

Polar Polymers in Polar Solvents

Some of the polymer samples would not dissolve in nonpolar solvents. Although the use of polar solvents introduced theoretical complications, some measurements were made on such systems. Table I shows some results obtained for solutions at a 10% concentration.

Nonpolar Polymers in Nonpolar Solvents

Systems of nonpolar polymers in nonpolar solvents would not be expected to show changes in dielectric constant due to orientation. Voet (8), however,

TABLE I

POLAR POLYMERS IN POLAR SOLVENTS

A. CELLULOSE ACETATE BUTYRATE IN CHLOROFORM.

B. CELLULOSE ACETATE IN 1:2 BUTYL ACETATE: TOLUENE.

C. POLYVINYL FORMAL IN CHLOROFORM.

A		B		C	
$G(\text{sec.}^{-1})$	$\frac{\Delta\epsilon}{\epsilon_s - \epsilon_0} \times 100$	$G(\text{sec.}^{-1})$	$\frac{\Delta\epsilon}{\epsilon_s - \epsilon_0} \times 100$	$G(\text{sec.}^{-1})$	$\frac{\Delta\epsilon}{\epsilon_s - \epsilon_0} \times 100$
200	-3.6	200	-2.2	172	-2.6
286	-9.0	389	-5.6	286	-5.1
400	-15.3	572	-10.0	400	-9.8
515	-20.6	800	-13.3	515	-14.9
600	-29.3			685	-18.9
715	-36.0	1141	-22.2	943	-28.9
858	-42.4	1370	-24.4	1030	-49.0
1060	-57.0	1695	-27.8	1200	-63.6

reported changes in the dielectric constants of solutions of polystyrene and polyisobutylene in toluene when these solutions were subjected to shear.

Our investigations of these systems failed to show any change of the dielectric constant under shear. It is also significant that the values of the dielectric constant determined for the solutions at rest differed markedly from those reported (8). Our measurements showed a linear relationship between the dielectric constant and the concentration expressed in volume per cent for these solutions. This contrasted with the sharp rise of the static dielectric constant reported after a critical concentration was reached (9).

Our data at 10 Kc., at 30°C. are shown in Fig. 4 for solutions of polystyrene of varying concentrations in toluene. Although samples of molecular weights of $10\text{--}13 \times 10^3$, $35\text{--}40 \times 10^3$, $65\text{--}70 \times 10^3$, and 100×10^3 were used, the experimental points plotted fall on a straight line. This is in essential

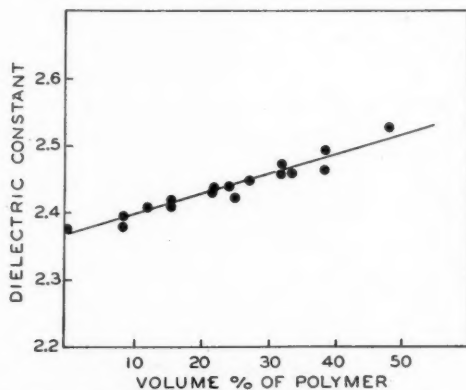


FIG. 4. Variation with concentration of rest dielectric constants of polystyrene of varying mol. wt. in toluene.

agreement with the Debye theory*. Our results have recently been mentioned by Voet in a subsequent note of correction (9).

Carbon Black Suspensions

In view of the marked discrepancy between our results on polymer solutions and those of Voet (7), it was of interest to check Voet's earlier measurements on the effect of shear on the dielectric constant of carbon black-mineral oil suspensions. A sample of printing ink obtained from the Canada Printing Ink Co. was used.

In this system large changes in dielectric constant were obtained at very low rates of shear. Changes in dielectric constant five times as great as those observed in polymer solutions were obtained at rates of shear 1/100th as great as those employed with the polymer solutions. Significant changes in the dielectric constant were observed at a rate of shear of less than 1 sec.⁻¹.

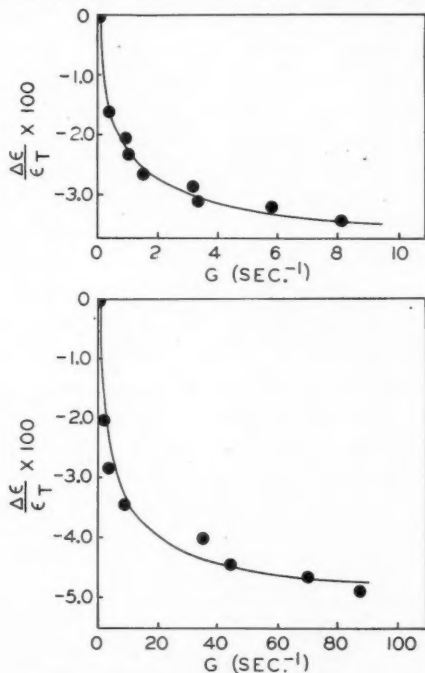


FIG. 5. Effect of rate of shear upon the dielectric constant of carbon black printing ink. Note in the upper curve the large effect at low rates of shear.

The data exhibited an exponential relationship between the decrease in dielectric constant and rate of shear. Fig. 5 shows some of the results obtained. The results are expressed as percentage changes: $\Delta\epsilon$ represents the change in dielectric constant under shear, and ϵ_T the total dielectric constant of the suspension at rest.

* (Added in proof.) P. Debye and F. Bueche. *J. Phys. & Colloid Chem.* 55: 235. 1951, have recently reported substantially the same results as those in Fig. 4.

Liquid Crystals

The anisotropy of liquid crystals in their transition region is well known. It therefore seemed worthwhile to investigate whether a change in dielectric constant under shear occurred in these systems, and for this purpose *p*-azoxyanisole was used. The sample possessed a melting point of 117°C. and a transition point of 132°C.

Dielectric measurements under shear were carried out at 100 and 300 Kc. at temperatures of 122°C. It was not found possible to work at lower frequencies or lower temperatures. At lower frequencies the high conductance of the liquid crystals interfered with the measurements of the dielectric constant. At lower temperatures difficulties were encountered owing to the freezing of the crystals in the bearings of the rotating condenser.

Nevertheless, the measurements were performed in the transition region, and near the melting point of the crystals. On subjecting the system to shear it was found that the bridge balance was disturbed. A careful analysis of many measurements, however, showed that the effect was due to a change in the conductance and that no significant change in the true capacitance of the system occurred up to velocity gradients of 1500 sec.⁻¹. It was therefore concluded that the oriented groups were too small to be affected by the shear gradients employed.

Discussion

The results, in general, support the picture of orientation in a shear gradient opposing the orientation in an electric field. For nonpolar polymers where no orientation in an electric field was to be expected no changes were observed.

It should be noted that, with one exception, all systems in which any change in dielectric constant occurred showed decreases in dielectric constant under shear. With ethyl cellulose in benzene, however, an increase in dielectric constant with increasing rate of shear was observed. This would indicate that the orienting effects of the electric field and of the mechanical shear were supplementary. Such a condition could exist if the polar groups of ethyl cellulose were perpendicular to the long axis of the molecules.

It is obvious from the experimental results that the picture is complicated by factors other than orientation. The slow return of the dielectric constant to its original value after rotation had ceased is shown in Fig. 3. If orientation were the only factor, the recovery would, in principle, have been instantaneous. This slow recovery, similar to that often observed for viscosity, probably arises from molecular interaction. Since polymer concentrations of from 10 to 30 gm. per 100 ml. of solvent had to be employed to obtain sufficient sensitivity of measurement, a high degree of particle interaction could be expected.

Under such conditions, considerations of photoelastic behavior may be applicable. For an amorphous linear polymer the mechanical effect of a stress

is shown in a series of retarded elastic effects in addition to the instantaneous elastic response. The total elastic strain is thus a function of time as well as of stress (4).

The instantaneous response can be regarded as resulting from an elastic strain. By analogy with the photoelastic phenomena this corresponds to a general stretching, with neighboring atoms being pulled apart slightly. This introduces a degree of anisotropy which would be evident as a double refraction corresponding to a change of refractive index in two directions perpendicular to one another. Similarly it can be regarded as giving rise to two dielectric constants perpendicular to one another, of slightly differing magnitudes.

The retarded photoelastic response is regarded as resulting from a time dependent segmental diffusion of the polymer chains. An uncurling and orientation of the polymer chains gives rise to further configurational strains and leads to additional anisotropy. The most significant of such configurational strains is believed to be due to orientation of relatively short segments of molecular chains.

We thus see that, as with streaming birefringence or photoelastic behavior, we may regard the changes in dielectric constant under shear as due to partial orientation of polymeric chains. Although the phenomenon of streaming birefringence lends itself to simpler theoretical treatment, the photoelastic effect seems to offer a basis for a more complete explanation of the experimental data.

Ostwald's conception of "strukturviskosität" (5, 6) appears to support the above views. As an example, the shearing of a dispersion of elastically deformable particles will produce a change in particle shape which will make flow progressively easier, and hence lower the viscosity. The particles need not be elastic. They may be polar and tend, when the system is at rest, to orientate themselves into some type of ordered structure which has to be destroyed before flow can take place. When the stress is removed the particles recover their original orientation. If this recovery is relatively slow, thixotropic behavior may be observed.

With suspensions of carbon black the changes in dielectric constant under shear were very pronounced. The results confirm Voet's work (8) on such systems, and the interpretation is probably best approached as suggested by him. In essence the latter's "agglomeration factor" can be regarded as derived from Ostwald's concept of structural viscosity due to the formation of molecular aggregates.

Acknowledgment

We wish to express our indebtedness to Miss Ruth Seidman for preparation of the sample of *p*-oxyanisole.

References

1. BURGERS, J. M. Second report on viscosity and plasticity. Academy of Sciences, Amsterdam. pp. 113 *et seq.* 1938.
2. EDSALL, J. T. Advances in colloid science. Vol. 1. Interscience Publishers Inc., New York. 1942.
3. GOODEVE, C. F. Trans. Faraday Soc. 35: 342. 1939.
4. KURTZ, S. S., HARVEY, W. T., and LIPKIN, M. R. Ind. Eng. Chem., Anal. Ed. 11: 476. 1939.
5. OSTWALD, W. Koll. Z. 38: 261. 1926.
6. PHILLIPPOFF, W. Koll. Z. 75: 142. 1936.
7. VOET, A. J. Phys. & Colloid Chem. 51: 1037. 1947.
8. VOET, A. J. Phys. & Colloid Chem. 53: 597. 1949.
9. VOET, A. J. Phys. & Colloid Chem. 54: 1070. 1950.

INFLUENCE OF ALCOHOLS UPON THE UNCATALYZED REACTION BETWEEN RESORCINOL AND FORMALDEHYDE¹

BY R. A. V. RAFF² AND B. H. SILVERMAN³

Abstract

The rate of the condensation of an uncatalyzed, equimolecular solution of resorcinol and formaldehyde in water was determined at 60°C. By replacing a portion of the water in this system with aliphatic alcohols, a reduction in the rates of condensation was noted at the same temperature. However, these reaction rates were found to vary widely among themselves, depending on the alcohol used. These results are explained under the assumption of the intermediate formation of hemiacetals from the free formaldehyde and the alcohols. The retarding effect of these alcohols on the resorcinol-formaldehyde condensation is inversely related to their different tendency to form esters with acids, or acetals with aldehydes, as reported by other authors. The general importance of the formation of hemiacetals is emphasized where formaldehyde is applied in the presence of alcohols.

Discussion of Previous Experiments

Previous work (15) on the kinetics of the uncatalyzed reaction of resorcinol and formaldehyde had shown the considerably higher reactivity of resorcinol as compared to phenol and to alkylated monophenols. For the various temperatures and the different ratios of resorcinol to formaldehyde which were investigated, a first order reaction rate constant served best to represent the experimental data. These condensations had been studied on solutions of resorcinol in dioxane and water, to which the calculated amounts of aqueous formaldehyde solutions were added. The charges were prepared in such a way that the combined weights of resorcinol plus formaldehyde (as CH₂O) represented 40% of the total weight of the solutions; the dioxane amounted to 26.7%; 33.3% water was present, partially introduced as part of the aqueous formaldehyde solution. These mixtures were reacted in a resin flask kept in a constant temperature bath, and the progress of the reaction determined from the gradual decrease in free formaldehyde on samples removed during the experiment.

Influence of Solvents

Since it appeared of interest to learn the influence of solvents upon the reaction rate of the uncatalyzed resorcinol-formaldehyde condensation, equimolecular mixtures of resorcinol and formaldehyde were reacted at 60°C., in which the dioxane in the above formulation was replaced by various aliphatic alcohols. One experiment was also carried out in an all aqueous medium, replacing the dioxane by water. As found in dioxane, a first order reaction rate constant served best to represent the experimental data.

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The solvents used, together with their densities and viscosities, are given in Table I, in the order of increasing reaction rate constants. The values for the pH's obtained for the reaction mixtures at the start and at the end of each experiment are shown to have remained practically unchanged.

Comparing the reaction rate of the condensation in water with the reaction rates obtained in the presence of the various alcohols, the retarding effect of the latter on the condensation rate is quite pronounced. A comparison of the alcohols among themselves shows that their retarding effect decreases from methyl alcohol to normal propyl alcohol, and still further to isopropyl alcohol and tertiary butyl alcohol.

These facts suggest the connection between the retarding effect of these alcohols on the condensation reaction and their molecular structures, involving the reactivity of the alcoholic hydroxyl groups.

Comparison with Esterification Reaction

A reaction of alcohols which is known to involve the alcoholic hydroxyl group and to be dependent upon the structure of the alcohol is the esterification reaction.

Kailan and coworkers (5,6,7,8,9,10) measured the esterification of a number of alcohols in a large surplus of different acids by determining the changes in the melting points of the mixtures during the reaction. Reaction rate constants obtained in measuring the uncatalyzed esterification of the alcohols with which the present work is concerned, in formic and acetic acids, are shown in Table I. From these data it appears that the more easily an alcohol is esterified, the more it retards the uncatalyzed resorcinol-formaldehyde condensation.

Comparison with Acetalization Reaction

Considering that, according to the accepted modern mechanism, the rate-controlling step in the esterification of carboxylic acids is the addition of the alcohol to the carboxylic carbonyl group, this indirect relationship between the retarding effect of the alcohols upon the condensation reaction and their tendency to form esters suggests the possibility that the alcohols take part in the resorcinol-formaldehyde condensation by forming intermediates with the free formaldehyde. The greater the reactivity of the hydroxyl group in an alcohol, the greater should be its tendency to bind temporarily the free formaldehyde, and the greater its retarding effect upon the resorcinol-formaldehyde condensation.

Reaction products between alcohols and aldehydes are known as acetals and hemiacetals. As far as the formation of acetals is concerned, a comparison of data by Minné and Adkins (13) actually indicates that the conversion to acetals from the various alcohols and acetaldehyde decreases with the tendency of the alcohols to retard the uncatalyzed resorcinol-formaldehyde condensation. This is shown in Table I and graphically represented in Fig. 1.

TABLE I
COMPARISON OF DATA ON SOLVENTS

Name	Solvent Formula	Density (20°) (4°)	Viscosity (c.p.s., 25°)	Resorcinol- formaldehyde condensation		Esterification		Acetal	
				$K \times 10^4$	pH Initial Final	K in formic acid	$K \times 10^4$ in acetic acid	Formation K^{**} with acetaldehyde(13)	Hydrolysis $K \times 10^3$ acidic(17)
Methyl alcohol	$\text{CH}_3 - \text{OH}$	0.791	0.547	2.7	3.52	3.46	12.3 ₍₆₎	2.41, 1.95	1.53
Ethyl alcohol	$\text{CH}_3 - \text{CH}_2 - \text{OH}$	0.789	1.006	4.7 ₍₄₎	3.45	3.45	8.4 ₍₆₎	1.40, 1.21	13.0
Normal propyl alcohol	$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{OH}$	0.803	1.967	5.3	3.55	3.53	9.4 ₍₆₎	1.06	14.4
Allyl alcohol	$\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{OH}$	0.855	1.215	5.7	3.62	3.58	4.6 ₍₁₀₎	0.84	Not measured
Iso propyl alcohol	$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CH} - \text{OH} \\ \diagup \\ \text{CH}_3 \end{array}$	0.783	2.06	7.5	3.51	3.53	2.1 ₍₆₎	0.10, 0.11	72.3
Tert. butyl alcohol	$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CH}_3 - \text{C} - \text{OH} \\ \diagup \\ \text{CH}_3 \end{array}$	0.789	4.47	8.6	4.00	3.72	Not measured	0.015, 0.019	Not measured
Water	$\text{H} - \text{OH}$	0.998	0.894	25.0	3.48	3.43	—	—	—

(*) The corresponding value for phenol has been determined as $K = 4.5 \times 10^{-3}$. **Equilibrium constant.

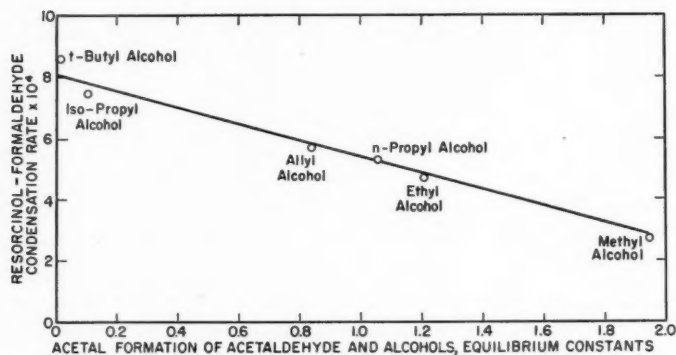


FIG. 1. Rates of resorcinol-formaldehyde condensation vs. equilibrium constants for acetal formation.

Accordingly, there appears to be a direct relationship between the data given by Skrabal and Eger (17, 12) on the acidic saponification of the acetals of some of the alcohols under discussion and their retarding effect. The slower the hydrolysis of an acetal, the greater the retarding effect of the related alcohol on the uncatalyzed resorcinol-formaldehyde condensation. This is borne out by the data shown in Table I and in Fig. 2.

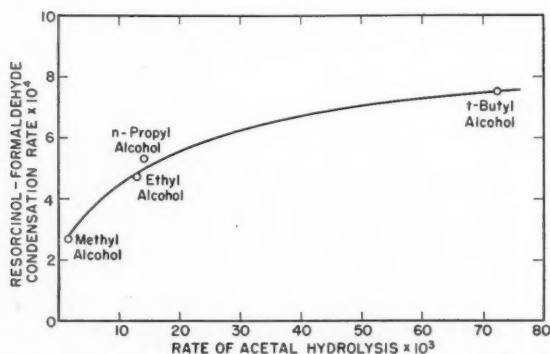


FIG. 2. Rates of resorcinol-formaldehyde condensation vs. rates of acetal hydrolysis.

Intermediate Formation of Hemiacetals as the Rate Governing Factor

Although evidence makes it seem likely that the intermediate reaction of formaldehyde with the alcohols is the rate governing reaction when the uncatalyzed resorcinol-formaldehyde condensation is carried out in the presence of these alcohols, the question of whether acetals or hemiacetals are the intermediates remains open.

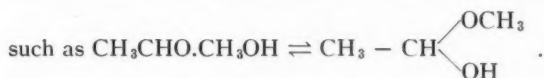
To decide between these two possibilities, an experiment was carried out in which an attempt was made to react resorcinol in water by adding formal (methylal), as the source of formaldehyde. Since hardly any condensation reaction took place under this condition, the acetal appears too stable a compound under the prevailing reaction conditions to occur as an intermediate product.

On the other hand, if "Methyl Formcel" (Celanese Corporation of America), a hemiacetal of methanol and formaldehyde, was used as a potential source of formaldehyde in uncatalyzed condensations with resorcinol, the condensation proceeded at the same speed as if the formaldehyde had been added in its free state as an aqueous solution.

It may, therefore, be concluded that hemiacetals and not acetals are the intermediate products if the uncatalyzed resorcinol-formaldehyde condensation is carried out in the presence of alcohols.

Literature Review on Hemiacetals

The formation of hemiacetals from alcohols and acetaldehyde was postulated from refractive indices and densities of such mixtures by Adkins and Broderick (1), and by Schimmel & Co. (16). Abnormalities in the ultraviolet absorption spectra of alcohols and aqueous solutions of carbonyl compounds were assumed by Herold (3) to be due to hemiacetal formation. The extent of this reaction was estimated from absorption measurements and linked with the molecular structure of both components. These ideas were further developed in a paper by Grabowsky and Herold (2) where the reaction mechanism of the hemiacetal formation is discussed on the basis of absorption measurements of alcohol and aldehyde solutions in inert solvents. Hemiacetal formation is considered by Mueller (14) as an intermediate step in the acetal formation and explained by the distribution of the electrons in the aldehyde. Herold and Wolf (4) measured the rate of hemiacetal formation in several aldehyde-alcohol systems by ultraviolet absorption experiments. With propionaldehyde, the rate of reaction was found to decrease in the order: methyl alcohol, ethyl alcohol, butyl alcohol, leading to equilibria containing increasing amounts of aldehyde. These results agree basically with the fact that methanol has a stronger retarding effect on the uncatalyzed resorcinol-formaldehyde condensation than ethanol. Whereas Herold and Wolf found the acetaldehyde-methanol reaction to proceed too rapidly for exact measurements by their method, Lauder (11) investigated this system at 0°C. by the use of a refractometer. He concludes that a reversible reaction, first order in each direction, occurs on mixing the reagents, and assumes that an equilibrium is set up between an alcoholate and the hemiacetal,



General Remarks

Aldehydes, particularly formaldehyde, are widely applied in the presence of alcoholic solvents. The moderating influence of alcohols in such reactions, the extent of which differs depending on their structure, has only been recognized in isolated cases, although it must be assumed to be of general occurrence and validity. It may be expected that such systems can be further modified by any variation in the amount of water present and by changes in the pH under which such reactions are carried out.

Acknowledgment

Thanks are due to Mr. C. D. Isack¹ for his assistance in the preparation of this paper. The support of this work by Koppers Company, Inc. and the permission by Dr. G. F. D'Alelio, Vice President of Koppers Company, Inc. to publish it are gratefully acknowledged.

References

1. ADKINS, H. and BRODERICK, A. E. J. Am. Chem. Soc. 50: 499. 1928.
2. GRABOWSKY, O. and HEROLD, W. Z. physik. Chem. B, 28: 290. 1935.
3. HEROLD, W. Z. Elektrochem. 39: 566. 1933.
4. HEROLD, W. and WOLF, K. L. Z. physik. Chem. B, 12: 165. 1931.
5. KAILAN, A. and ADLER, F. Monatsh. 63: 155. 1933.
6. KAILAN, A. and BRUNNER, G. Monatsh. 51: 334. 1929.
7. KAILAN, A. and FRIEDMANN, N. Monatsh. 62: 284. 1933.
8. KAILAN, A. and HAAS, W. Monatsh. 60: 386. 1932.
9. KAILAN, A. and RAFF, R. Monatsh. 61: 116. 1932.
10. KAILAN, A. and SCHWEBEL, S. Monatsh. 63: 52. 1933.
11. LAUDER, I. Trans. Faraday Soc. 44: 729. 1948.
12. LOEBERING, J. and FLEISCHMANN, A. Ber. B, 70: 1713. 1937.
13. MINNÉ, N. and ADKINS, H. J. Am. Chem. Soc. 55: 299. 1933.
14. MUELLER, A. Helv. Chim. Acta, 17: 1213. 1934; 19: 225. 1936.
15. RAFF, R. A. V. and SILVERMAN, B. H. Ind. Eng. Chem. 43: 1423. 1951.
16. SCHIMMEL & Co. BER. SCHIMMEL & Co. 1933, p. 78; Ann. Rept. 1933, p. 71.
17. SKRABAL, A. and EGER, H. H. Z. physik. Chem. 122: 349. 1926.

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ELECTRONIC INTERPRETATION OF THE UNCATALYZED REACTION BETWEEN RESORCINOL AND FORMALDEHYDE IN ALCOHOLS AND DIOXANE¹

By A. R. INGRAM²

Abstract

The condensation of resorcinol and formaldehyde in aqueous alcohols and dioxane is interpreted on the basis of competing electrophilic reactions of the hydroxymethyl carbonium ion with the resorcinol aromatic ring and with the oxygen atoms of the resorcinol and the solvents. The reaction of the carbonium ion and the alcohol groups leads to oxonium ions which may then form hemiacetals.

Introduction

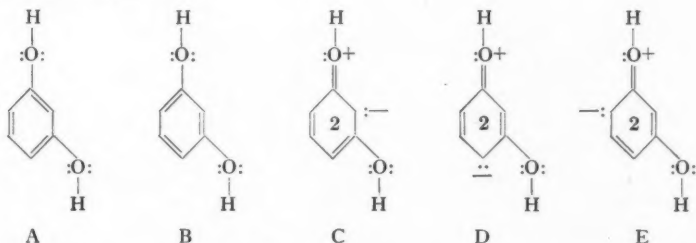
Raff and Silverman (15, 16) have determined the reaction rates of equimolar proportions of resorcinol and formaldehyde in water and in the aqueous solutions of dioxane, methyl alcohol, ethyl alcohol, normal-propyl alcohol, allyl alcohol, iso-propyl alcohol, and tertiary-butyl alcohol, at 60°C. and at pH values lying within the range of 3.5 to 4.0. The organic solvents were found to retard the condensation of resorcinol and formaldehyde and the effect of the alcohols was attributed to their reversible formation of hemiacetals with the formaldehyde.

In this paper an attempt is made to interpret all the reactions involved in terms of the electronic theory of acids and bases (1, 8, 10).

Resonance in Molecular and Ionic Resorcinol

A consideration of the most probable resonance structures of resorcinol is important in order to visualize the electronic distribution responsible for reaction.

(a) Un-ionized resorcinol

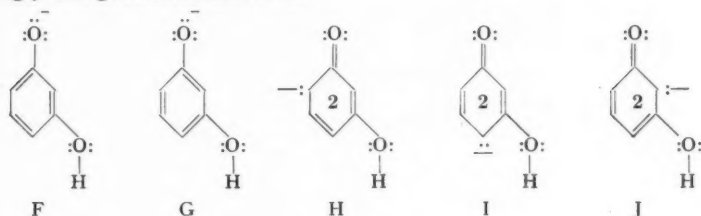


¹ Manuscript received May 21, 1951.

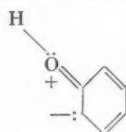
Contribution from the Mellon Institute of Industrial Research, Pittsburgh, Pa. (Multiple Fellowship on Special Resins, Koppers Company, Inc.).

² Fellow at Mellon Institute of Industrial Research, Pittsburgh, Pa.

(b) Singly charged resorcinolate ion



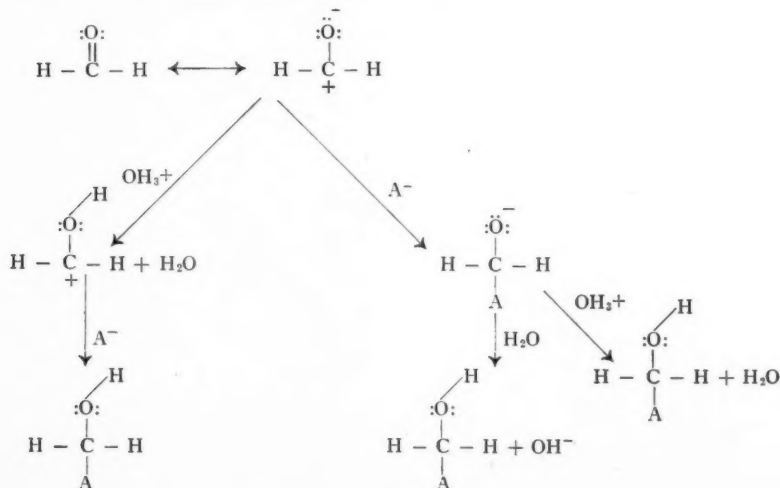
In the system under investigation it is believed that the resorcinolate ion structures represent best the resonance picture for the reactive resorcinol molecule involved in nuclear condensation with formaldehyde. According to Pauling (14), the resonance structures of phenol which involve separated

charges such as  are much less stable than the conventional

Kekulé structure and contribute only a small amount, 7 kcal. per mole to resonance energy. On the other hand, the resonance energy of the phenolate ion, corresponding to structures F through J with $-H$ in place of $-OH$, is about 8 kcal. per mole greater than that for un-ionized phenol.

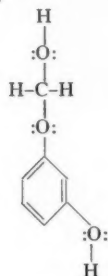
Formation and Reaction of Formaldehyde Carbonium Ion

Formaldehyde contains an extremely reactive carbonyl group, capable of reacting with centers of high electron density. In neutral or slightly acid media, these reactions are probable:



Reaction of Formaldehyde with Resorcinol at the Negative Oxygen Atom in the Resorcinol Ion

Where A^- is the resorcinolate ion, the formaldehyde may make an electrophilic attack at the phenolate oxygen of F or G or at the nucleophilic centers on H, I, or J. The reaction at the phenolate oxygen would then yield the monohemiformal of resorcinol, K.

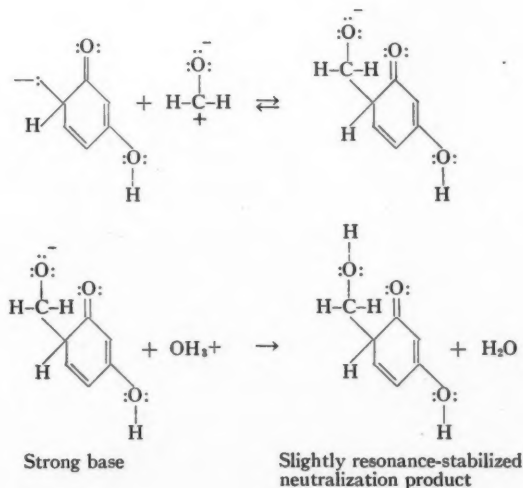


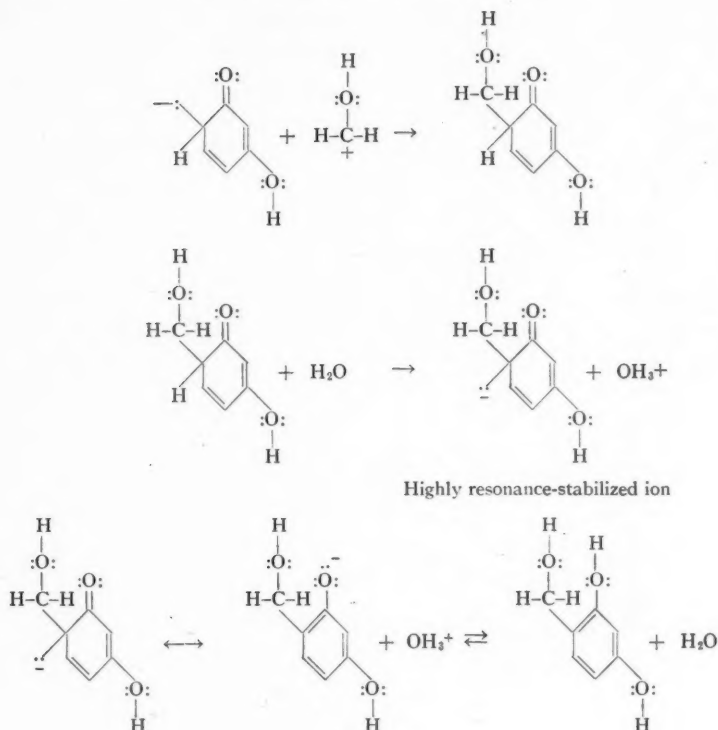
(K)

According to some authors (e.g. 2, 17) the hydroxymethyl group in the phenyl hemiformal, corresponding to K, may migrate to the ring. However, the hemiformal of phenol, because of its instability, has never been isolated.

Reaction of Formaldehyde Directly on the Aromatic Ring

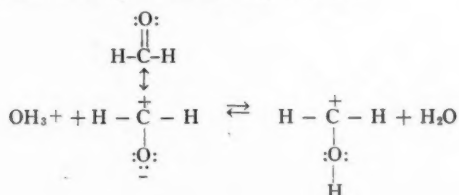
Since the attack of the carbonyl group in formaldehyde can occur directly on the electronegative 6-, 4-, or 2-positions in the stable electronic structures, H, I, and J (see below), the postulation of the hemiformal, K, as the important intermediate in the mechanism of nuclear hydroxymethylation seems unessential. The resorcinolate ion, H, is considered to react with formaldehyde as follows:





Effect of pH on Reaction Mechanism

It should be pointed out that the acidity of the system affects the mechanism by shifting the following two equilibria:



Thus, in strongly acid media, the concentration of resorcinolate ion will greatly diminish, but on the other hand the concentration of the hydroxymethyl carbonium ion will increase. In strongly basic media, the resorcinolate ion concentration will increase, and the carbonium ion concentration will decrease. Hultsch (4) has presented a mechanism for strongly acid catalyzed conden-

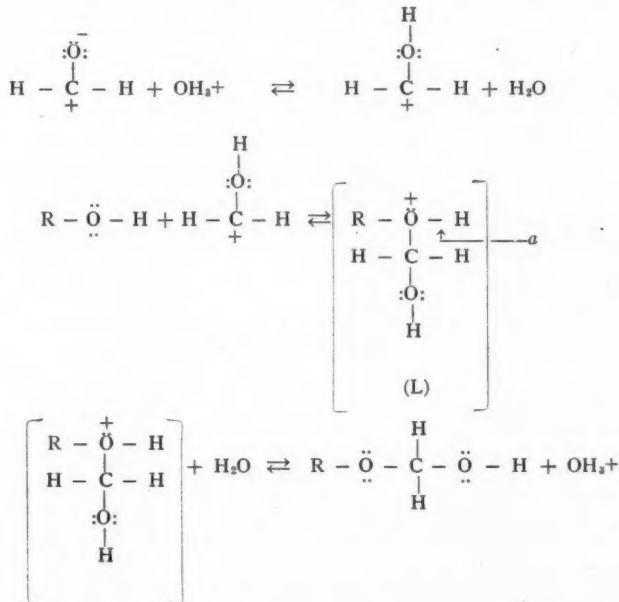
sation of phenol which involves the polarized form of the phenol (such as C through E for resorcinol) as the intermediate reacting through the aromatic

nucleus with the carbonium ion $\begin{array}{c} \text{OH} \\ | \\ \text{H} - \text{C} - \text{H} \\ + \end{array}$. In alkaline media Hultsch proposes an attack of the negative spots of the phenolate ion on the polarized carbonyl bond of formaldehyde.

Since the reactions studied by Raff and Silverman were carried out in mildly acid media, it is felt that the resonance stabilized ionic structure of resorcinol should play an important role in reacting with formaldehyde either as a carbonium ion or as a polarized carbonyl compound.

Retarding of Resorcinol-Formaldehyde Condensation by Alcohols

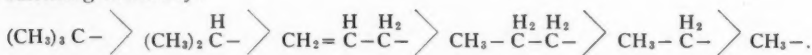
If there are added to the aqueous reaction medium, compounds such as alcohols or dioxane which have an electron sharing capacity due to the free electrons on the oxygen atoms, these compounds will then compete with the resorcinolate ion or molecular resorcinol for reaction with the formaldehyde. The reaction of alcohols was recognized by Raff and Silverman (16) as the reversible formation of a hemiacetal, equations for which are given below for reaction under mildly acid conditions:



It should be pointed out that R-O-H in the above mechanism includes not only the alcohol added to modify the resorcinol reaction but also represents resorcinol itself which is also competing with the resorcinolate ion. Reversible formation of hemiacetals, therefore, is felt to take place between resorcinol and formaldehyde as well as between the added alcohol and formaldehyde.

The mechanism of hemiacetal formation, according to Müller (12), involved splitting the alcohol into H^+ and OR^- , arising from a hydrogen bonding between the alcoholic hydrogen and the oxygen of the carbonyl group. The H^+ and OR^- then added to the carbonyl group. However, it seems much more plausible that the carbonyl group would first add the readily available proton originating from the free acid, thus giving rise to a carbonium ion which would attack the alcoholic oxygen to give a loosely bound oxonium ion, which could in turn eliminate a proton to form the hemiacetal.

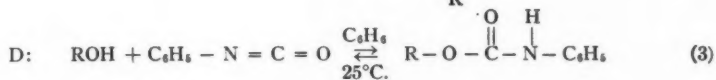
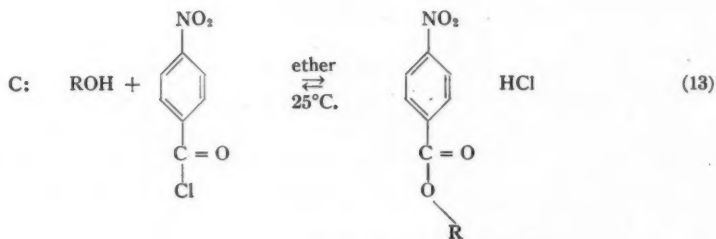
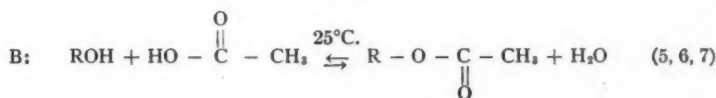
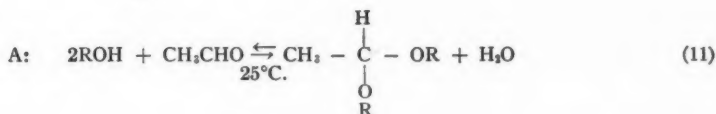
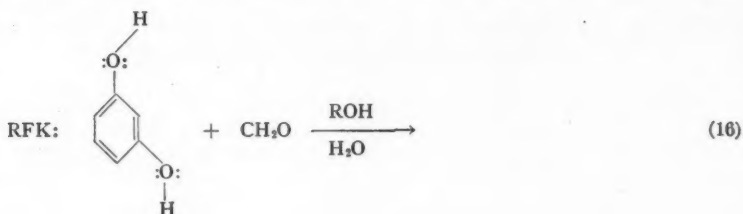
The tendency of an alcohol to form an acetal should be indirectly proportional to its electron releasing effect in the direction of the oxygen-hydrogen bond, a , in the oxonium complex L. The electron releasing power of the alkyl groups of the alcohols investigated are given in order of the decreasing electron releasing tendency:



This series is in the order of decreasing chain length, branching on the number one carbon, and unsaturation—all factors believed to contribute to electron release. From this series it would be expected that methanol would have the greatest tendency to form acetals and would retard the resorcinol-formaldehyde reaction the greatest. When the rate constants for the condensation of resorcinol and formaldehyde in the various alcohols were plotted by Raff and Silverman against the equilibrium constants of acetal formation as determined by Minné and Adkins (11), a remarkably precise linear inverse relationship was obtained. Other alcohol reaction rates such as those observed in reactions with acids (5, 6, 7), acid chlorides (13), or isocyanates (3) were similarly related to the resorcinol-formaldehyde condensation rate in the given alcohol. These reactions all involve rupture of the O-H bond. The data are summarized in Table I.

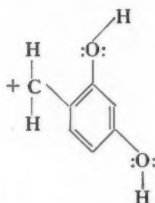
TABLE I
RELATION BETWEEN ALCOHOL MODIFIED RESORCINOL-FORMALDEHYDE
REACTION AND REACTIVITY OF THE ALCOHOLS

R -	Relative equilibrium constants	Relative rates			Rate constant $\times 10^4$
	A	B	C	D	RFK
CH_3-	1	1	1	1	2.6
C_2H_5-	0.555	0.459	0.96	0.68	4.7
$n-C_3H_7-$	0.486	0.358	0.78	0.76	5.3
$\overset{H}{\underset{ }{C}}-\overset{H_2}{\underset{ }{C}}-$	0.385	0.372			5.7
$i-C_3H_7-$	0.046	0.0549	0.31	0.17	7.3
$t-C_4H_9-$	0.008	0.0147	0.0032	Not determined	8.6



Effect of Alcohols on Polymeric Chain Growth

The further condensation of the methylol resorcinol with either another methylol group or an electronegative unsubstituted 2-, 4-, or 6- position would involve, according to Lilley (9) or Hultsch (4), electrophilic attack by the carbonium ion arising from the methylol group, i.e.



Alcohols present here would solvate this carbonium ion to give an oxonium complex, thereby retarding the chain growth of the resorcinol-formaldehyde polymer.

Retarding of Condensation by Dioxane and *t*-Butyl Alcohol Where Hemiacetal Formation is Restricted

Raff and Silverman did not attempt to explain in their papers (15, 16) the retarding effect of aqueous dioxane on the condensation of resorcinol and formaldehyde. Since dioxane is probably too stable to be ruptured by formaldehyde under these conditions, a chemical reaction in this sense is unlikely. However, the condensation rate was decreased from 25.0 to 10.5 by the addition of dioxane. Since dioxane is known to give stable oxonium compounds, Raff has previously suggested that this effect might be due to the formation of an oxonium compound with formaldehyde at the carbonium ion.

Since *t*-butyl alcohol exhibits practically no tendency to form acetals or to undergo other reactions involving a rupture of the oxygen to hydrogen bond, it would be expected, like dioxane, to retard the resorcinol-formaldehyde reaction mostly by reason of an oxonium complex ion like L. It is interesting to point out that the first order resorcinol-formaldehyde condensation rate in dioxane is 10.5×10^{-4} , compared to 8.6×10^{-4} for *t*-butyl alcohol.

Acknowledgment

The encouragement of Dr. R. A. V. Raff to write this paper, the critical reading of the contents by Dr. R. Levine at the University of Pittsburgh, and the permission of Dr. G. F. D'Alelio, Vice President of the Koppers Company, for publication are gratefully acknowledged.

References

1. ALEXANDER, E. R. Principles of ionic organic reactions. John Wiley and Sons, Inc., New York. 1950.
2. BRESLAUER, J. and PICTET, A. Ber. 40: 3785. 1907.
3. DAVIS, T. L. and FARNUM, J. M. J. Am. Chem. Soc. 56: 883. 1934.
4. HULTZSCH, K. Chemie der Phenolharze. Springer-Verlag, Berlin. 1950. pp. 24, 25.
5. KAILAN, A. and HAAS, W. Monatsh. 60: 386. 1932.
6. KAILAN, A. and RAFF, R. Monatsh. 61: 116. 1932.
7. KAILAN, A. and SCHWEBEL, S. Monatsh. 63: 52. 1933.
8. LEWIS, G. N. Valence and the structure of atoms and molecules. Chemical Catalog Company, New York. 1923.
9. LILLEY, H. S. J. Soc. Chem. Ind. (London), 67: 196. 1948.
10. LUDER, W. F. and ZUFFANTI, S. The electronic theory of acids and bases. John Wiley and Sons, Inc., New York. 1946.
11. MINNÉ, N. and ADKINS, H. J. Am. Chem. Soc. 55: 299. 1933.
12. MÜLLER, A. Helv. Chim. Acta, 19: 225. 1936.
13. MORRIS, J. F. and ASHDOWN, A. A. J. Am. Chem. Soc. 47: 837. 1925.
14. PAULING, L. The nature of the chemical bond. Cornell University Press, Ithaca, N.Y. 1948. pp. 163, 164.
15. RAFF, R. A. V. and SILVERMAN, B. H. Ind. Eng. Chem. 43: 1423. 1951.
16. RAFF, R. A. V. and SILVERMAN, B. H. Can. J. Chem. 29: 857. 1951.
17. WALKER, J. F. Formaldehyde. Reinhold Publishing Corp., New York. 1944. pp. 163, 164.

COMPONENT FATTY ACIDS OF RAPESEED OIL¹

BY C. G. YOUNGS, T. M. MALLARD, B. M. CRAIG,
AND H. R. SALLANS

Abstract

The fatty acid composition of the oil from Argentine rapeseed grown in Western Canada was investigated by converting the glyceride esters to methyl esters and distilling the latter in a Podbielniak Heligrad distillation column. Analyses of the fractions showed 6 to 10% more eicosenoic acid and 7 to 10% less erucic acid than was previously reported for rapeseed oils.

The compositions of rapeseed and other Cruciferae oils have been the subject of a number of investigations in recent years (1, 2, 3, 4, 5, 6) and erucic, oleic, linoleic, and linolenic acids have been established as major constituents in these oils. Hopkins (5) first showed the presence of eicosenoic acid in hare's-ear mustard oil and more recent work (2, 6) has confirmed the presence of this acid in rapeseed oil.

Hydrolysis of rapeseed oil liberates acids which differ both in chain length and in degree of unsaturation. A complete fatty acid analysis requires an initial separation on the basis of chain length or unsaturation. A number of workers have obtained partial separation by distillation of the methyl or ethyl esters and further analyses were based on heart cuts of these fractions. Norris and Terry (7) indicated that the Podbielniak Heligrad distillation unit (8) effected nearly complete separation of these esters. A similar unit was used in the present investigation.

Rapeseed oil obtained from Prairie Vegetable Oils Ltd., Moose Jaw, Sask., was alkali refined and bleached to give a clear golden yellow oil.

The methyl esters were first prepared according to the following conventional procedure. The oil was saponified with alcoholic potassium hydroxide and the fatty acids were liberated with sulphuric acid. The fatty acids were washed free of mineral acid and converted to the methyl esters by refluxing with methanol containing 1% of concentrated sulphuric acid. The yields obtained varied from 88 to 96%, with a free fatty acid content of 1 to 2%. Quantitative recovery (99.4%) of the acids as their methyl esters was, however, obtained by converting the soaps to methyl esters with dimethyl sulphate (10). The free fatty acid content of the product was 0.2%. The esters prepared by the dimethyl sulphate procedure were divided into two portions, one of which was hydrogenated to an iodine value of 0.3 units. A small amount (0.02%) of N.D.G.A. was added to the nonhydrogenated esters prior to distillation.

A Podbielniak Heligrad distillation unit with a 25 mm. by 3 ft. column was used for the distillation. The column was operated at a head pressure of 10 mm.,

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a pressure drop across the column of 10 mm., and a reflux setting of 15 to 1. Adiabatic conditions were closely approached by covering the vacuum jacket of the column with an electrically heated mantle maintained at a temperature just below that at the head of the column.

The analytical values of the original oils and esters are given in Table I. Fig. 1 shows the distillation curves for the hydrogenated and nonhydrogenated esters prepared by the dimethyl sulphate procedure. Cuts between the fractions were made at the beginning of each transition. The material which distilled over during each transition represented about 1% of the total sample. The weights per cent of the corresponding fractions of hydrogenated and nonhydrogenated esters agreed within 0.3%, indicating that there was negligible carry over of the unsaturated esters due to association. The first three fractions, the C₁₆, C₁₈, and C₂₀ esters, were collected and the pot fraction was assumed to be C₂₂ esters.

TABLE I
ANALYTICAL VALUES OF OIL AND ESTERS

	Original oil	Conventional esters		Original oil	Dimethyl sulphate esters	
		Found	Calc.*		Found	Calc.*
Iodine value	105.1	104.6	104.7	104.7	103.9	104.2
Saponification value		175.8		174.3	174.0	173.8
Unsaponifiable, %	0.7	0.7	0.7	0.8	0.8	0.8
Linolenic, %	9.2	9.2	9.2	8.7	8.5	8.7
Linoleic, %	15.1	14.5	15.1	15.7	15.7	15.7
Yield of esters, %		88	100		99.4	100
Free fatty acid, %		0.8	0		0.2	0

* Calculated from the values found for the original oil.

The analytical values of the distilled fractions of the esters prepared both by the conventional and dimethyl sulphate procedures are given in Table II. The diene and triene acids were determined by ultraviolet analysis (9), using a Beckmann Model DU spectrophotometer. Iodine values were measured by the Wijs method with one-half hour reaction time. Weights per cent and saponification values for fractions from the hydrogenated esters are included in Table II for comparison. In Table III the weighted totals of the analytical values found for the distilled fractions are compared to the values for the original esters. A small amount of destruction of the diene and triene acids occurred during the distillation, which was verified by the slight decrease in iodine value. The amounts destroyed were of the order of 0.5% which would not materially affect the final acid analysis.

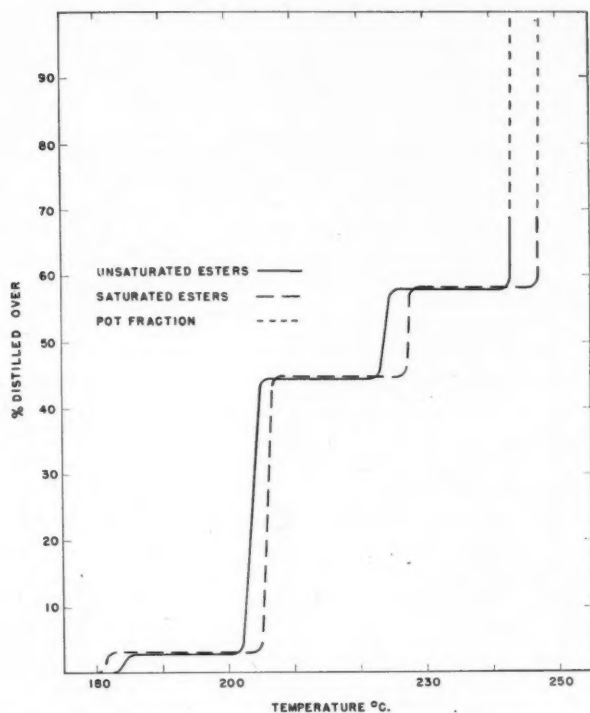


FIG. 1. Distillation curves for hydrogenated and nonhydrogenated methyl esters of rapeseed oil prepared by dimethyl sulphate procedure.

TABLE II
ANALYTICAL VALUES OF DISTILLED FRACTIONS

	Weight %	Iodine value	Saponi- fication value	Triene acid, %	Diene acid, %
Fraction 1					
Conventional	2.7	23.3	208.7	3.4	1.4
(Me) ₂ SO ₄	2.9	23.3	206.7	3.8	3.2
Hydrogenated	3.1	—	208.6	—	—
Fraction 2					
Conventional	41.2	145.5	191.2	18.7	33.1
(Me) ₂ SO ₄	41.5	145.9	189.9	19.2	33.1
Hydrogenated	41.7	—	187.8	—	—
Fraction 3					
Conventional	13.7	87.1	175.7	4.6	4.1
(Me) ₂ SO ₄	13.4	83.2	173.5	2.4	5.1
Hydrogenated	13.3	—	171.8	—	—
Fraction 4					
Conventional	42.4	74.2	156.6	—	0.9
(Me) ₂ SO ₄	42.2	73.9	156.2	—	1.6
Hydrogenated	41.9	—	154.8	—	—

TABLE III
COMPARISON OF PROPERTIES OF ORIGINAL ESTERS WITH SUMMATION OF
DISTILLED FRACTIONS

Property	Dimethyl sulphate		Conventional	
	Original esters	Total from fractions	Original esters	Total from fractions
Iodine value	103.9	103.6	104.6	104.0
Saponification value	174.0	174.0	175.8	174.9
Diene acid, %	15.69	15.19	14.50	14.50
Triene acid, %	8.54	8.41	9.20	8.40
Naturally conj. diene	0.21	0.40	0.26	0.45
Naturally conj. triene	0.16	0.02	0.02	0.01

Table IV summarizes the distribution of the acids in the four fractions on the basis of the whole oil. Diene and triene acids in Fractions 1 and 3 were considered to be linoleic and linolenic acids which carried over from Fraction 2. The diene acid in Fraction 4 was considered to be docosadienoic acid. The amounts carried over in all cases were small on the basis of the whole sample, so that carry over of acids other than linoleic and linolenic was neglected. The monoethenoid acids in Fractions 1, 2, 3, and 4 were taken as hexadecenoic, oleic, eicosenoic, and erucic, respectively. The amount of each acid was calculated from the iodine value of the fraction and the diene and triene acid content. The saturated acids, palmitic, stearic, arachidic, and behenic were

TABLE IV
DISTRIBUTION OF THE ACIDS IN FRACTIONS

Fatty acid	Percentages*									
	Fraction 1		Fraction 2		Fraction 3		Fraction 4		Total	
	Conven.	Me ₂ SO ₄	Conven.	Me ₂ SO ₄	Conven.	Me ₂ SO ₄	Conven.	Me ₂ SO ₄	Conven.	Me ₂ SO ₄
Palmitic	2.1	2.4							2.1	2.4
Hexadecenoic	0.3	0.2							0.3	0.2
Linoleic		0.1	13.6	13.7	0.6	0.7			14.2	14.5
Linolenic	0.1	0.1	7.7	8.0	0.6	0.3	0.8	.008	9.2	8.4
Oleic			15.7	15.4					15.7	15.4
Stearic			2.3	2.5					2.3	2.5
Arachidic					0.7	0.8			0.7	0.8
Eicosenoic					11.2	11.0			11.2	11.0
Behenic							0.9	1.3	0.9	1.3
Erucic							37.8	37.6	37.8	37.6
Docosadienoic							0.4	0.7	0.4	0.7
Unsaponifiable							1.8	1.9	0.7	0.8

* Calculated on the basis of whole oil.

determined by difference. Small amounts of lignoceric acid have been reported in rapeseed oil by Hilditch (2) and Kapur (6). In view of the small amount of saturated acid in Fraction 4 no attempt was made to establish the presence of this acid.

The values in Table IV were calculated to a fatty acid basis and are compared in Table V to data reported by Hilditch (2) and by Kapur (6) for other rapeseed oils. The erucic acid content is 7 to 10% lower and the eicosenoic acid content 6 to 10% higher in the present investigation. The value for eicosenoic acid is of the same magnitude as that reported by Hopkins (5) for hare's-ear mustard seed oil.

TABLE V
COMPARISON OF FATTY ACID COMPOSITIONS OF RAPESEED OIL

Acid	Hilditch(2)	Kapur(6)	Present investigation*	
			Conventional	Me ₂ SO ₄
Myristic		0.6		
Palmitic	2.6	1.0	2.2	2.5
Hexadecenoic	0.6		0.3	0.2
Stearic	1.0	0.2	2.4	2.6
Oleic	16.0	17.7	16.6	16.3
Linoleic	12.5	13.8	15.0	15.3
Linolenic	9.9	9.1	9.7	8.9
Arachidic	0.6	0.4	0.7	0.8
Eicosenoic	6.0	3.1	11.8	11.6
Behenic	2.1	2.6	1.0	1.4
Erucic	47.3	50.4	39.9	39.7
Docosadienoic	0.9		0.4	0.6
Lignoceric	0.5	1.2		

* Calculated to fatty acid basis.

The close agreement between the fatty acid analysis of the esters prepared by the two methods indicates that although only an 88% yield was obtained by the conventional procedure a representative sample of esters was obtained. The presence of unsaturated acids did not appreciably affect the separation obtained by fractional distillation as shown by the weight per cent of corresponding fractions from the hydrogenated and nonhydrogenated esters. This, coupled with the small loss of diene and triene acids, would indicate an error in the final analysis of less than 1% for the major constituent acids.

References

1. BALIGA, M. N. and HILDITCH, T. P. *J. Soc. Chem. Ind. (London)*, 67: 258. 1948.
2. HILDITCH, T. P., LAURENT, P. A., and MEARA, M. L. *J. Soc. Chem. Ind. (London)*, 66: 19. 1947.
3. HILDITCH, T. P. and PAUL, H. *J. Soc. Chem. Ind. (London)*, 54: 331T. 1935.
4. HILDITCH, T. P., RILEY, T., and VIDYARTHI, N. L. *J. Soc. Chem. Ind. (London)*, 46: 457. 1927.
5. HOPKINS, C. Y. *Can. J. Research, B*, 24: 211. 1946.
6. KAPUR, S. L. and DAUBERT, B. F. *J. Am. Oil Chemists' Soc.* 26: 472. 1949.
7. NORRIS, F. A. and TERRY, D. E. *Oil & Soap*, 22: 41. 1945.
8. PODBIELNIAK, W. J. *Ind. Eng. Chem. Anal. Ed.* 13: 639. 1941.
9. Report of the Spectroscopy Committee. *J. Am. Oil Chemists' Soc.* 26: 399. 1949.
10. YOUNGS, C. G. and CRAIG, B. M. To be published.

THE ADDITION COMPOUNDS OF SILICON TETRACHLORIDE AND AMINES¹

By W. R. TROST

Abstract

Addition compounds formed between silicon tetrachloride and some amines have been prepared and analyzed. Molecular ratios of 4/1, 2/1, and 1/1 were established for amine to silicon tetrachloride in these compounds. It is suggested that these molecular compounds use $4s$, $3d$, $4p$ orbitals only, in forming the coordinate bonds that establish the compound, and that the configuration of the silicon tetrachloride remains essentially undisturbed. Use of these assumptions permits definite structural predictions to be made about the compounds.

In preliminary experiments with silicon tetrachloride and amines, the formation of addition compounds was noted whenever an amine was mixed with silicon tetrachloride. The following amines were used: diethylamine, triethylamine, butylamine, dibutylamine, tributylamine, piperidine, morpholine, ethanolamine, diethanolamine, pyridine, dimethylaniline, and aniline. When silicon tetrachloride was added to excess amine, in the ratio of 1/10 by volume, a voluminous usually white precipitate formed, extensive enough to transform the liquid mixture into a grease. When amines were added to excess silicon tetrachloride, in the ratio of 1/10 by volume, colored solids (frequently yellow) precipitated from the colorless liquid. These exothermic reactions occurred as rapidly as the mixing process, but the large heat of reaction varied considerably, seeming to decrease with the strength of the base and with the number of hydrogen atoms on the amine nitrogen. The compounds, once formed, could be kept indefinitely with no further change.

Of these compounds, those derived from pyridine, aniline, and dimethylaniline could be most conveniently analyzed.

Experimental

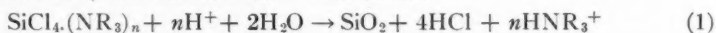
The addition compounds of pyridine, aniline, and dimethylaniline with silicon tetrachloride were prepared by mixing equimolar solutions of the amines and the chloride with each other in varying ratios by volume. The reactants, with petrol ether or benzene as solvents, were kept as cold as was possible without a change in phase. Because they react with moist air, the molecular compounds that formed were analyzed in the solvent. They were also analyzed as dry solids, for these could be recovered by filtering and washing the precipitates in an atmosphere of nitrogen, followed by complete drying *in vacuo*. The same analytical method was used for the analyses of the addition compounds, whether they were dry solids, or were still immersed in anhydrous solvent.

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Analysis

The addition compounds decompose in dilute aqueous acid giving silica, hydrochloric acid, and the acid salt of the amine.



If the amines² are bases whose dissociation constants have values between 10^{-6} and 10^{-10} , the strong and weak acids in the mixture resulting from the decomposition Equation (1) can together be analyzed by means of a two end-point titration using standard sodium hydroxide and the indicators methyl orange and phenolphthalein. Each mole of silicon tetrachloride produces four moles of hydrochloric acid. Silicon tetrachloride was therefore equated to one-quarter of the net increase in acidity resulting from the decomposition and measured at the phenolphthalein end point.

$$\text{Moles SiCl}_4 = \frac{\text{Moles (base - acid)}}{4} \quad (2)$$

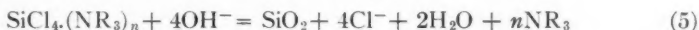
The amine was identified with the amount of base needed to carry the mixture from a methyl orange to a phenolphthalein end point.

$$\text{Moles NR}_3 = \text{moles base (methyl orange to phenolphthalein)} \quad (3)$$

The mole ratio, n , was obtained from (2) and (3)

$$n = \frac{\text{Moles NR}_3}{\text{Moles SiCl}_4} \quad (4)$$

The net result of the acid decomposition and the two end-point titration with the base was



Pyridine, aniline, and dimethylaniline are bases whose constants have suitable values for the analysis. The method was confirmed for these amines by titrating known mixtures of silicon tetrachloride and amine, and by titrating knowns of each of the amines and of silicon tetrachloride separately.

Addition Compounds with Pyridine

Pyridine and silicon tetrachloride were made up as 1.74 *M* solutions in petrol ether. The two solutions were combined in different volume ratios. The precipitate that formed was centrifuged and washed repeatedly with petrol ether until all free amine and chloride had been removed. The solid, still immersed in petrol ether, was next decomposed by 25.00 ml. 0.1500 *N* hydrochloric acid, and the decomposed mixture titrated with 0.1000 *N* sodium hydroxide to methyl orange and phenolphthalein end points. The results of these analyses are presented in Table I. The composition of the solution in which the reaction occurred is given in the first three columns, and the composition of the precipitate resulting from the reaction is recorded in the last three columns.

A. $\text{SiCl}_4(\text{Pyridine})_2$

The data for the analysis of the diaminate are given for the compound as it occurs in the solvent (Table I), and as a dry solid (Table IV). This yellow

²NR₃ is used to represent any amine.

TABLE I
ANALYSIS OF $\text{SiCl}_4(\text{PYRIDINE})_n$ PRECIPITATES IN PETROL ETHER

Reaction mixture			Precipitate			
Pyridine SiCl ₄	Moles $\times 10^3$		Moles $\times 10^3$		Pyridine SiCl ₄	Color
	Pyridine	SiCl ₄	Pyridine	SiCl ₄		
1/39	0.348	13.55	0.35	0.17	2.1/1	Yellow
1/11	0.348	3.83	0.34	0.17	2.0/1	Yellow
1/7	1.10	7.70	1.08	0.53	2.0/1	Yellow
1/3	1.74	5.22	1.39	0.73	1.9/1	Yellow
5/3	4.35	2.61	4.27	1.94	2.2/1	Mixed
3/1	5.22	1.74	4.07	1.72	2.4/1	Mixed
6/1	6.00	1.00	2.53	0.94	2.7/1	Mixed
19/1	6.61	0.35	0.97	0.27	3.6/1	Mixed
39/1	13.55	0.35	1.42	0.36	4.0/1	White
50/1	43.5	0.87	2.39	0.61	3.9/1	White
100/1	97.5	0.97	1.48	0.37	4.0/1	White

microcrystalline compound was recovered from silicon tetrachloride and pyridine solutions mixed in the ratio of 12/1. The dry yellow solid quickly turns white in moist air, and then liquifies, while acid fumes are given off. In dry air, decomposition begins at about 100°C., accompanied by acid odors, the darkening of the solid which ends up as an ash, and the appearance of a colorless liquid that freezes into white crystals.

B. $\text{SiCl}_4(\text{Pyridine})_4$

This compound is a white powder, soluble in pyridine and hygroscopic, adding water quickly to become a white odorless grease. All of the water except about two molecules per mole can be easily removed. When heated the compound does not melt, but begins to decompose at about 200°C., giving some pyridine among other products, and leaving an infusible ash. The analyses for this compound are reported in Tables I and IV.

Addition Compounds with Dimethylaniline

When dimethylaniline is added to silicon tetrachloride in such a way that no mixing occurs, the diffusion of the two liquids into one another quickly establishes three distinct zones in the interface region. The bottom zone consists of a flocculent pink precipitate which slowly curls off to fall through the liquid silicon tetrachloride. Above this a curdy, olive green precipitate forms, while a thick yellow agglomeration colors the third zone which fades into the liquid amine above. The separation and suspension of the three zones, as diffusion proceeds, is maintained by the different densities of the precipitates, but the pink compound is just heavy enough to collect in the silicon tetrachloride phase. This is fortunate, as the pink compound adds more amine and turns green when the amine concentration is more than about 0.2% of the chloride. The analyses of these three addition compounds, recorded in Table II, identifies the pink precipitate as the monoaminate, the green precipitate as the diaminate, and the yellow precipitate as the tetraminate.

TABLE II

ANALYSIS OF $\text{SiCl}_4(\text{Me}_2\text{ANILINE})_n$ PRECIPITATES IN PETROL ETHER

Reaction mixture			Precipitate			
$\frac{\text{Me}_2\text{Aniline}}{\text{SiCl}_4}$	Moles $\times 10^3$		Moles $\times 10^3$		$\frac{\text{Me}_2\text{Aniline}}{\text{SiCl}_4}$	Color
	$\text{Me}_2\text{Aniline}$	SiCl_4	$\text{Me}_2\text{Aniline}$	SiCl_4		
1/100	0.25	25	0.26	0.25	1.0/1	Pink
1/100	0.25	25	0.18	0.14	1.3/1	Pink
1/100	0.25	25	0.24	0.245	1.0/1	Pink
1/14	0.87	12.2	0.375	0.190	2.0/1	Green
14/1	12.2	0.87	0.34	0.084	4.0/1	Yellow

A. $\text{SiCl}_4(\text{Me}_2\text{Aniline})_1$

The pink compound was prepared in pure silicon tetrachloride and analyzed in petrol ether (Table II), and as a dry solid (Table IV). The monoaminate decomposes when heated, giving off acid fumes, and changing color from pink to yellow at about 80°C. No liquid appears and the final product is a gray powder. The compound reacts with water vapor, turning orange and giving acid fumes.

B. $\text{SiCl}_4(\text{Me}_2\text{Aniline})_2$

The green compound prepared in petrol ether (Table II) turns red when dried (Table IV) but the color change does not affect the composition. Both forms are, analytically, diamines. On heating, the red compound gives off acid fumes and turns yellow at about 70°C. It then melts, and its subsequent decomposition is much like that of the tetramine. On exposure to water vapor, the red compound turns yellow, becomes greasy, and gives acid fumes.

C. $\text{SiCl}_4(\text{Me}_2\text{Aniline})_4$

A yellow addition compound analyzed in petrol ether (Table II) or as a dried solid (Table IV) was identified as the tetramine. This compound, like the diamine, shows two colors. The yellow solid, refluxed at 60°C. for one hour in a mixed petrol ether-cyclohexane solvent containing excess dimethylaniline, transformed into a brown product. The analysis of the brown form was similar to that of the yellow (Table IV). Both are soluble in dimethylaniline and neither give color to the solution. Both behave in the same way on heating, changing into thick brown liquids at about 65°C. that become thin enough to run at about 80°. Further heating causes frothing, amine odors, and another color change from brown to green. Colorless liquids distill off and very strong odors develop. In moist air, both forms melt, change color, and pick up water at about the same rate, and similarly lose it until about two molecules of water per mole remain.

Addition Compounds with Aniline

When aniline is added to a large excess of silicon tetrachloride a transient red precipitate appears. This compound, which might be the monoaminate, could not be recovered. Apart from this, yellow and white solids were prepared and analyzed.

A. $\text{SiCl}_4(\text{Aniline})_2$

The yellow precipitate, analyzed in benzene (Table III) and as a dry solid (Table IV) corresponds to the diaminate. It reacts quickly with water vapor turning white and giving acid fumes.

TABLE III
ANALYSIS OF $\text{SiCl}_4(\text{ANILINE})_n$ PRECIPITATES IN BENZENE

Reaction mixture			Precipitate			
$\frac{\text{Aniline}}{\text{SiCl}_4}$	Moles $\times 10^3$		Moles $\times 10^3$		$\frac{\text{Aniline}}{\text{SiCl}_4}$	Color
	Aniline	SiCl_4	Aniline	SiCl_4		
1/30	2.0	60.0	1.62	0.82	2.0/1	Yellow
14/1	12.2	0.87	2.25	0.57	4.0/1	White

TABLE IV
ANALYSIS OF $\text{SiCl}_4(\text{NR}_3)_n$ AS DRY SOLIDS

Compound	Analysis			Mass balance		Color
	Moles $\times 10^3$		Amine SiCl ₄	Grams weighed	Grams found	
	Amine	SiCl ₄				
SiCl ₄ .(Pyridine) ₂	1.16	0.546	2.12/1	0.1818	0.1805	Yellow
SiCl ₄ .(Pyridine) ₄	2.17	0.545	3.98/1	0.2700	0.2650	White
SiCl ₄ .(Me ₂ Aniline) ₁	0.249	0.243	1.02/1	0.0705	0.0710	Pink
SiCl ₄ .(Me ₂ Aniline) ₂	0.394	0.202	1.95/1	0.0812	0.0825	Red
SiCl ₄ .(Me ₂ Aniline) ₄	3.39	0.850	3.98/1	0.5540	0.5560	Brown
SiCl ₄ .(Me ₂ Aniline) ₄	0.889	0.221	4.02/1	0.1452	0.1459	Yellow
SiCl ₄ .(Aniline) ₂	0.909	0.429	2.12/1	0.1610	0.1575	Yellow
SiCl ₄ .(Aniline) ₄	2.47	0.620	3.99/1	0.3335	0.3345	White

B. $\text{SiCl}_4(\text{Aniline})_4$

The white precipitate, analyzed in benzene (Table III), or as a white powder (Table IV), confirms the tetraminate formula. The compound is unaffected by water vapor, neither gaining nor losing weight in the course of several days exposure. On heating, it begins to decompose at about 185°C., giving aniline hydrochloride and leaving an infusible ash.

Stability of the Addition Compounds

All of the addition compounds are indefinitely stable when kept in dry air, or in an anhydrous inert solvent. But few of them have enough stability to manage a phase change. The thermal decompositions are complicated processes though they may begin simply, when the amine nitrogen carries no hydrogen, with a partial regeneration of chloride and amine. The diamines and the monamine give heavy acid fumes at temperatures below 100°C., and leave large ashes. The tetramines decompose at temperatures below 200°C. Amines, or amine hydrochlorides, appear together with other products and a substantial ash is left. Exposed to water vapor the diamines undergo disruptive chemical reactions which may indicate the addition of water to the exposed silicon tetrachloride, for hydrogen chloride is eliminated. The compounds with four amine groups may add water when exposed to the vapor but are not apparently degraded by it. The diamines react with excess amine to form the tetramines. The tetramines dissolve in excess amine. In summary, the tetramines are more stable and less reactive than the corresponding diamines.

The Structures of the Addition Compounds

It will be assumed that the analyses definitely establish³ the occurrence of the compounds $\text{SiCl}_4(\text{NR}_3)_1$, $\text{SiCl}_4(\text{NR}_3)_2$ and $\text{SiCl}_4(\text{NR}_3)_4$. In addition, the compound $\text{SiCl}_4(\text{NH}_3)_6$ is known (2). An attempt to explain the valences and predict the structures of these molecular compounds will be made.

In dealing with the structures and valences shown by complex ions, it is usually sufficient to treat all of the bonding orbitals as a group, and to find, from the resonance among them, that stable hybrid configuration that will explain the properties of the complex (1). But this method may not be satisfactory when applied to the molecular compounds formed between silicon tetrachloride and the amines. For the most part, the bonds that establish the chloride-amine compounds can probably be thought of as coordinate bonds in which electron-pairs from nitrogen atoms fill vacant orbitals in the silicon atom. The possibility for resonance among these bonds and the covalent Si-Cl bonds is not promising. On the one hand, it would be required that 3s, 3p orbitals mix with 4s, 3d, 4p orbitals, and on the other, that the asymmetry introduced by the amine molecules (as compared to the chlorine atoms) still be overcome. In addition, a coordination number of 10, which is thought to be impossible for silicon, would have to be explained if the hexammonate is included. Again, the steric implication that the already crowded silicon tetrachloride molecule can add extra groups into itself is so unlikely as to practically eliminate the argument.

³The reviewer has drawn the attention of the author to the work of A. Hardin, *J. Chem. Soc.*, 51: 40, 1887, who reported 2:1 addition compounds between pyridine and silicon tetrachloride, and quinoline and silicon tetrachloride.

The molecule silicon tetrachloride has tetrahedral symmetry and uses four sp^3 bonds. This gives silicon an electron structure $3s^2 3p^6$, and requires silicon to use $4s$, $3d$, $4p$ orbitals if it is to become involved in further bonding. Because of the electronegativity of the chlorine atoms, the unused silicon orbitals ($4s$, $3d$, $4p$) would be expected to be more available in silicon tetrachloride than in other silicon compounds, excepting silicon tetrafluoride. Specifically, the group theoretical treatment (1) states that there are two d orbitals in silicon tetrachloride that can form two strong π bonds, plus an additional two d orbitals that can form two weak π bonds, and that the Si-Cl bonds themselves achieve some double bond character, for unshared pairs from the chlorine atoms are thought capable of forming π bonds by occupying the d orbitals of the silicon. This description might lead to the expectation that silicon tetrachloride would form a stable addition compound with two amine groups, and perhaps also an unstable addition compound with n equal to 4. These predictions are not fulfilled by the amine compounds, for the tetramine is more stable than the diamine and in addition monoamine and hexamine addition compounds occur.

Considering these difficulties, it is suggested that the amine groups add to the silicon tetrachloride molecule by using stablest hybrids from the $4s$, $3d$, $4p$ silicon orbitals, that no mixing occurs with the $3s$, $3p$ orbitals, and that silicon tetrachloride retains its sp^3 configuration. This would permit the formation of stronger coordinate bonds at greater distances from the silicon atom. In addition, only deformations of a secondary type (molecule-dipole interactions, etc.) would be required in the silicon tetrachloride molecule as amine groups add to it. In a way, the silicon tetrachloride molecule can be thought of as an atom, with the amine groups adding to form an envelope around it. It is assumed that the $4s$, $3d$, $4p$ orbitals of silicon provide the usual hybrid orbitals (1).

$\text{SiCl}_4(\text{NR}_3)_1$

The silicon orbital from $4s$, $3d$, $4p$ that will form the most stable bond with one electron-pair is $4s$. This would not be, in itself, a directed bond. But greater penetration, with a corresponding increase in stability, would result if the amine molecule approached the silicon tetrachloride in the direction of the center of one of the faces of the tetrahedron. This could lead to some distortion, principally displacements of the three chlorine atoms. Some definition in structure would therefore be expected, the amine group being long bonded and opposite one chlorine atom, with the other three chlorine atoms pushed up out of their tetrahedral positions. The molecule should have a large dipole moment.

$\text{SiCl}_4(\text{NR}_3)_2$

The ds configuration would be the stablest for two bonds. This is an angular arrangement, suggesting the possibility that both amine groups could approach tetrahedral faces. Molecule-dipole interactions should cause some distortion in the silicon tetrachloride. The resulting molecular compound would have a

large dipole moment, as it lacks symmetry with regard to the distribution of electrons. Alternatively, however, the bonds could be called d^2 bonds. This arrangement is also angular (1), and would correspond to the amines' use of the two strong d orbitals supposedly resident in the normal silicon tetrachloride molecule.

$SiCl_4.(NR_3)_4$

For four bonds the d^3s is the stablest selection from the $4s$, $3d$, $4p$ group. This is a tetrahedral arrangement (1) which will be satisfied if the four amines are imagined to sink into the hollows in the four faces of the silicon tetrachloride tetrahedron. A description of the structure of the molecular compound would be that of a large tetrahedron (the four amine groups) enclosing a small tetrahedron (silicon tetrachloride). The two tetrahedra would be so rotated that the corners of one were perpendicular to the faces of the other. Because of its symmetry, the tetramine would not be expected to have a dipole moment.

$SiCl_4.(NR_3)_6$

Six bonds formed from s , p , d , orbitals almost always have the octahedral d^2sp^3 arrangement (1). This would enable each amine in the hexamine to approach an edge of the silicon tetrachloride tetrahedron and to lodge, as it were, in the hollow between two chlorine atoms; d^3s could also accommodate six bonds, but this arrangement is irregular (1). If d^2sp^3 is correct, the addition compound would possess no permanent dipole moment.

For all of these compounds it has been assumed that the Si-Cl bonds retain their sp^3 character. They will necessarily lose whatever double bond properties they possess, however, when the addition compounds form, and might be expected for this reason to become weaker and longer.

References

1. KIMBALL, G. E. J. Chem. Phys. 8: 188. 1940.
2. ROCHOW, E. G. Chemistry of the silicones. John Wiley and Sons, Inc., New York. 1946.

PHYSICAL CONSTANTS AND ESTIMATION OF STEREOISOMERIC 2,3-BUTANEDIOLS¹

By R. W. WATSON, J. A. R. COOPE, AND J. L. BARNWELL

Abstract

The refractive index-temperature relation for optically active and *racemic* diols is linear, with $n_D^{25} = 1.4310 - 0.00036(t - 25)$ from 25° to 40°C.; for the *meso*-isomer $n_D^{25} = 1.4372 - 0.00034(t - 25)$ from 25° to 50°C. The specific rotation $[\alpha]_D^{25} \cong \pm 13.2^\circ$. Measurements of n_D^t and α_D^t in suitably purified mixtures of stereoisomers allow calculation of the percentage of each isomer present. Tests of the method on known mixtures of all three stereoisomers show an experimental error of $\pm 3\%$. Analyses of five diol samples from pilot plant fermentations of beet molasses by *Aerobacter aerogenes* reveal 65-87% *meso*-, from 2 to 16% *dextro*-, and from 0 to 33% *racemic* 2,3-butanediol.

Refractive indices from 1.4306 to 1.4322 at 25°C. have been reported for optically active and *racemic* 2,3-butanediols. Wide variations also occur in the recorded values of specific rotations and densities as shown in Table I. Specific rotations for the *levo*-isomer reportedly range from -12.85° to -13.34° . The present investigation aims to establish more accurate values for these constants and to develop a simple physical method, based on their use, for rapid estimation of isomeric ratios.

Two methods for the estimation of isomers in mixtures of isomeric 2,3-butanediols have been described in the literature. Tipson (16) successfully used the procedure of conversion to isopropylidene derivatives followed by fractional distillation. The *meso*-derivative was readily separated in this way. Robertson and Neish (13) described a method in which the isomers in a 1 gm. sample were converted to their di-*p*-nitrobenzoates by a modified Schotten-Baumann reaction, dissolved in chloroform, measured polarimetrically to determine the concentration of optically active isomers, and fractionally crystallized for estimation of relative amounts of *dl*- and *meso*-esters. Four to six crops of crystals provided 90 to 95% recovery, from which the different components were separated by hand and weighed. This method has the unique advantage of simultaneously identifying the isomers, although several days are required for a determination. A simple procedure is described in the present communication which requires only 0.5 gm. of suitably purified diol, is accurate to $\pm 3\%$, and may be completed within half an hour.

The variations noted in the reported values of physical constants have probably arisen from measurements on impure or mixed isomers. Removal of acids, esters, ketones, and ketals as well as prevention of isomerization and absorption of water comprise the main difficulties in obtaining the pure com-

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* $t = ^\circ\text{C}$.

TABLE I

PREVIOUSLY REPORTED PHYSICAL CONSTANTS OF STEREOISOMERIC 2,3-BUTANEDIOLS

Isomer Constant	levo-	Ref.	dextro-	Ref.	racemic	Ref.	meso-	Ref.
Refractive index	$n_D^{25} = 1.4307$	19	$n_D^{25} = 1.4306$	7	$n_D^{25} = 1.4310$	11	$n_D^{25} = 1.4364$	14
	$n_D^{25} = 1.4308$	3					$n_D^{18} = 1.4387^*$	8
	$n_D^{25} = 1.4309$	7					$n_D^{25} = 1.4384^*$	19
	$n_D^{25} = 1.4310$	22, 20					$n_D^{35} = 1.4324$	7
	$n_D^{26} = 1.4318$	9					$n_D^{35} = 1.4325$	10
	$n_D^{18} = 1.4340$	8						
Specific rotation	$[\alpha]_D^{23} = -12.85$	8			$[\alpha]^{26} = 0.000$	10	$[\alpha]_D^{20} = +0.80^*$	3
	$[\alpha]_D^{25} = -13.0$	19					$[\alpha]_D^{25} = +1.0^*$	19
	$[\alpha]_D^{20} = -13.1$	3					$[\alpha]_D^{25} = +1.06^*$	8
	$[\alpha]_D^{25} = -13.17$	5						
	$[\alpha]_D = -13.19$	7						
	$[\alpha]_D^{26} = -13.34$	10						
Density and specific gravity	$d_{20}^{20} = 0.992(2)$	3	$d^{25} = 0.9872$	7			$d^{20} = 1.0033$	14
	$d_4^{25} = 0.9873$	3					$d^{20} = 1.004$	10
	$d^{25} = 0.9069$	7					$d^{25} = 0.990$	8
	$d_{15}^{26} = 0.9880$	9					$d^{25} = 0.9939$	7
	$d_{30}^{30} = 0.983(8)$	3						
	$d_{40}^{40} = 0.9750$	3						

*Aerobacter diol.

pounds. The preparation of stereoisomeric diols of high purity is described in the experimental section. All purified samples gave negative tests for acetyl groups (2), esters (4), ketones, and ketals (6). Water contents, estimated by the Karl Fischer method (15) did not exceed 0.046%. Accurately determined physical constants of the isomers are reported in Table II.

Close agreement between the refractive indices of optically active and *racemic* diols prepared by different methods (Table II) is evidence for their accuracy to the fourth place. The value of n_D^{25} for the *dextro*-, *levo*-, and *racemic* forms is therefore 1.4310. The refractive index of *meso*-diol at 25°C. was obtained by direct reading on the supercooled liquid. The same value (± 0.0001) is obtained (a) by extrapolation of readings on a series of *meso*-dl-

TABLE II
PHYSICAL CONSTANTS OF STEREOISOMERIC 2,3-BUTANEDIOLS
FOUND IN THE PRESENT INVESTIGATION

Isomer	<i>levo</i> -			<i>racemic</i>		<i>meso</i> -
	Sample A	Sample B	Sample C	Sample A	Sample B	
Water, %	0.046	0.028		0.040		0.042
Constant						
Refractive index n_D^{25}	1.43095	1.43100	1.4310	1.43109	1.43095	1.43719
Optical rotation α_D^{25} (1 dm.)	-12.75	-12.73	-12.99	-0.005	0.00	0.00
Specific rotation $[\alpha]_D^{25}$	-12.92	-12.90	-13.16	-0.005	0.00	0.00
Density d_4^{25}	0.9873					

and *meso-levo*- mixtures (Fig. 1) as well as (b) by extrapolation of a series of readings on the pure diastereoisomer at temperatures above the melting point (Fig. 2). The value of n_D^{25} for *meso*-diol is therefore 1.4372 ± 0.0001 .

Changes in refractive index with temperature have not previously been determined. Values of n_D^{25} for the *racemic*, *levo*-, and *meso*-forms over the range from 25° to 50°C. are given in Table III. These readings are plotted versus

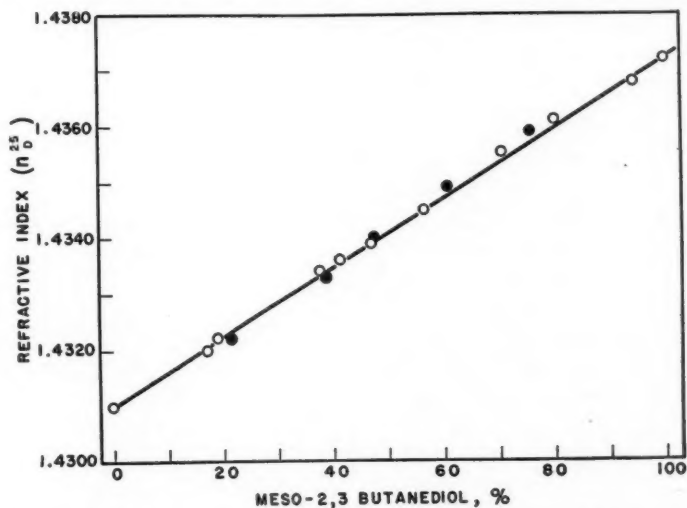


FIG. 1. Refractive index vs. per cent *meso*-2,3-butanediol in *meso-levo*-mixtures (open circles) and *meso-dl*-mixtures (solid circles).

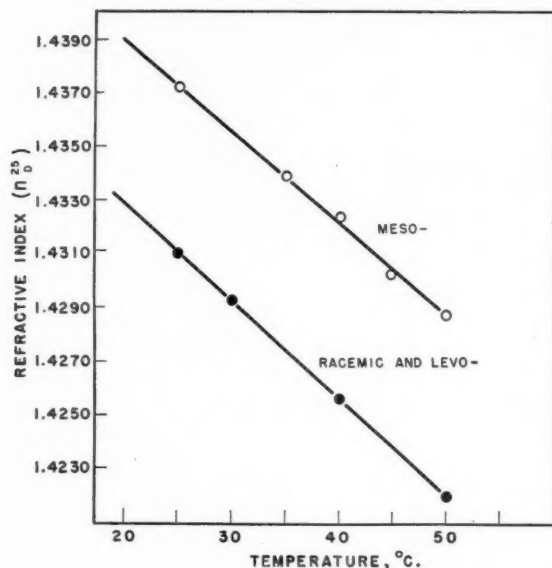


FIG. 2. The temperature-refractive index relation for racemic, levo-, and meso-2,3-butanediols.

temperature in Fig. 2 and show strictly linear relations. Conversion coefficients for the refractive indices of (a) *levo*- and *racemic* forms from 25° to 40°C. and (b) the *meso*-isomer from 25° to 50°C. are therefore -0.00036 and -0.00034 respectively per degree Centigrade rise in temperature.

The specific rotation $[\alpha]_D^{25} = -12.92^\circ$, obtained for the first supposedly pure sample (A, Table II) of *levo*-diol was viewed with suspicion. The experience of other investigators indicated that this value was probably too low (see Table I). Accordingly the entire procedure of preparation and purification was repeated, with care being taken to prevent metal contamination and isomerization (21). Polarimetric measurement of the second sample (B, Table II) merely served to confirm the value obtained for the specific rotation of Sample A. A third sample, prepared with special care from an-

TABLE III
REFRACTIVE INDICES OF ISOMERS AT VARIOUS TEMPERATURES

Temp., °C.	<i>levo</i> -	<i>racemic</i>	<i>meso</i> -
25	1.4310	1.4310	1.4372
30	1.4293	1.4293	
35			1.4339
40	1.4256	1.4256	1.4323
45			1.4303
50	1.4220	1.4220	1.4287

other fermentation of wheat by *B. polymyxa* (23) had $n_D^{25} = 1.4310$, $[\alpha]_D^{25} = -13.16^\circ$. In view of the fact that the refractive indices of these three samples are almost identical it seems probable that *B. polymyxa* produces a small variable amount of the *dextro*-isomer and that the true specific rotation is nearer -13.16° (9). The recent work of Garner and Lucas (5) gives $[\alpha]_D^{25} = -13.17^\circ$ for the *levo*-isomer. Although this constant cannot yet be accepted as established, any error which may remain in its measurement is too small to effect a variation of more than $\pm 2\%$ in the results of a physical method for the estimation of isomeric ratios.

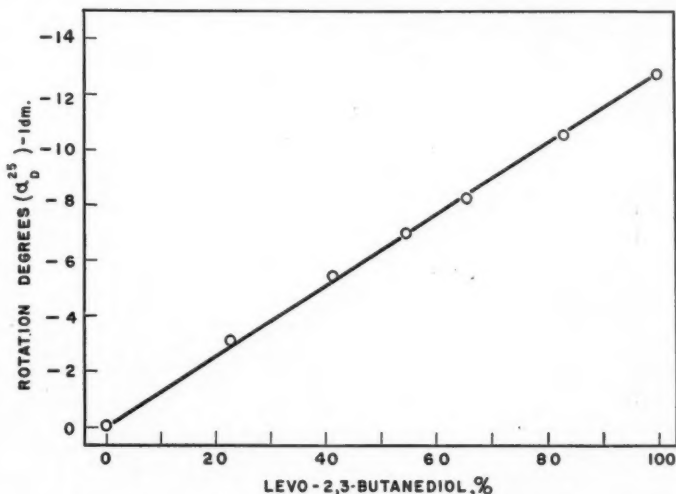


FIG. 3. Relation between optical rotation and per cent levo-2,3-butanediol in meso-levo-mixtures.

The density of the pure *levo*-isomer was stated by Clendenning (3) to be $d_4^{25} = 0.9873$. Repetition of this measurement using Sample A of *levo*-diol exactly confirmed the previous determination as shown in Table II. Moreover, the value reported for the density of *dextro*-diol is almost identical (see Table I), so that $d_4^{25} = 0.9873$ was used in calculations of the specific rotation.

The refractive indices of a series of *meso-levo*- and *meso-dl*- mixtures are given in Tables IV and V respectively. These values are plotted in Fig. 1 and show a linear relation between concentration and refractive index at 25°C . The weight per cent of *meso*-2,3-butanediol in a mixture of stereoisomers whose D-line refractive index at 25.0°C . = x may therefore be calculated from the expression,

$$\% \text{ meso} = \frac{x - 1.4310 \times 100}{0.0062}$$

The comparatively narrow gap of 0.0062 divisions between the refractive indices at 25°C . of the internally compensated and other isomers makes

TABLE IV
 REFRACTIVE INDICES OF *meso-levo*-MIXTURES

No.	<i>levo</i> -, gm.	<i>meso</i> -, gm.	<i>levo</i> -, %	<i>meso</i> -, %	n_D^{25}
1	100.0	...	100.0	0.0	1.4310
2	3.1350	0.6471	82.9	17.1	1.4320
3	0.8799	0.2088	80.8	19.2	1.4322
4	2.3342	1.4113	62.3	37.7	1.4334
5	0.8919	0.6263	58.7	41.3	1.4336
6	0.6443	0.4552	58.6	41.4	1.4336
7	2.0422	1.8016	53.1	46.9	1.4339
8	1.6279	2.1102	43.5	56.5	1.4345
9	1.1632	2.8177	29.2	70.8	1.4355
10	0.1963	0.7897	19.9	80.1	1.4361
11	0.0518	0.8393	5.8	94.2	1.4368
12	0.0	100.0	0.0	100.0	1.4372

 TABLE V
 REFRACTIVE INDICES OF *meso-dl*-MIXTURES

No.	<i>dl</i> -, gm.	<i>meso</i> -, gm.	<i>dl</i> -, %	<i>meso</i> -, %	n_D^{25}
1	100.0	0.0	100.0	0.0	1.43102
2	1.0625	0.2934	78.4	21.6	1.43219
3	0.5471	0.3432	61.5	38.5	1.43334
4	0.4811	0.4353	52.5	47.5	1.43396
5	0.3326	0.5200	39.0	61.0	1.43486
6	0.3114	0.9676	24.4	75.6	1.43592
7	0.0	100.0	0.0	100.0	1.43719

accurate determination of the fourth place necessary. Without special precautions this may be obtained under ordinary conditions from a series of readings with an Abbé refractometer.

Specific rotation is independent of dilution (Fig. 3). Since errors in polarimetry need not exceed $\pm 0.02^\circ$, and a range of approximately 13.0° occurs between the rotations (1 dm.) of optically active and inactive diols, direct estimates of the percentage of an optically active isomer present in a mixture in excess of its enantiomer may be made with an error $< \pm 2\%$. The optical rotations (1 dm.) of a series of *levo-dl*-mixtures at 25°C . are shown in Table VI.

 TABLE VI
 OPTICAL ROTATIONS (1 DM.) OF *levo-dl*-MIXTURES

No.	<i>levo</i> -, gm.	<i>dl</i> -, gm.	<i>levo</i> -, %	<i>dl</i> -, %	α_D^{25}
1	0.0	100.0	0.0	100.0	0.00
2	0.8628	2.9149	22.8	77.2	-3.04
3	1.6648	2.3446	41.5	58.5	-5.32
4	2.1663	1.7983	54.7	45.3	-6.98
5	2.5917	1.3668	65.5	34.5	-8.30
6	3.3890	0.6834	83.2	16.8	-10.58
7	100.0	0.0	100.0	0.0	-12.74

These values are plotted in Fig. 3, and show a linear relation between concentration and optical activity. The weight per cent of either optically active isomer in a mixture whose optical rotation (1 dm.) at 25°C. = $\pm y$ may therefore be obtained from the equation:

$$\% \text{ optically active isomer} = \frac{\pm y \times 100}{\pm 13.0}$$

The percentage of the *racemic* mixture is obtainable by difference.

Tests of the method on mixtures containing all three stereoisomers, with refractive indices measured in room air, are reported in Table VII. The isomeric composition, calculated from measurements of the refractive index and optical rotation, are within $\pm 3\%$ of the known values.

TABLE VII
TEST OF METHOD ON KNOWN MIXTURES

No.	n_D^{25}	α_D^{25}	Known weight % of isomers in mixture			Weight % of isomers calculated from n_D^{25} and α_D^{25}		
			<i>levo</i> -	<i>dl</i> -	<i>meso</i> -	<i>levo</i> -	<i>dl</i> -	<i>meso</i> - %
1	1.4312	-5.29	41.4	56.8	1.8	41.5	55.2	3.2
2	1.4324	-3.68	29.8	49.0	21.2	28.9	48.5	22.6
3	1.4328	-3.82	30.6	40.9	28.5	31.4	39.6	29.0
4	1.4331	-4.86	40.0	28.9	31.1	38.2	27.9	33.9
5	1.4338	-2.42	20.7	37.1	42.2	19.0	35.8	45.2
6	1.4340	-5.99	50.9	2.4	46.8	47.0	4.7	48.3

The method was applied to the mixed 2,3-butanediols produced by *Aerobacter aerogenes*. Walpole (18) originally reported that this organism formed a *meso-racemic* mixture with a small positive rotation. Böeseken and Cohen (1) also showed that certain samples may contain an unstated percentage of the *racemic* mixture; and Tipson (16) recently reported the presence of D-(*levo*)-2,3-butanediol in the mixed 2,3-butanediols from the normal fermentation of glucose by *A. aerogenes*. Pilot plant samples of 2,3-butanediol, all obtained from the fermentation of beet molasses by *A. aerogenes* Strain M148, were purified (see experimental section). Karl Fischer determinations on two of the purified samples showed 0.02% and 0.065% of water respectively. Isomeric ratios obtained by the physical method were checked for one sample by fractional crystallization of the di-*p*-nitrobenzoyl esters. Results are shown in Table VIII. The percentage of *racemic* diol reported by the ester method for Sample 2 is known to be too high because of the difficulty of removing fine *meso*-crystals from *dl*-buttons. The proportion of *meso*-diol reported by the physical method varies from 65-87%, of the *dextro*- isomer from 2 to 16%, and of the *racemic* mixture from 0 to 33%. Whether this variation exists in the diol produced by the organism, or whether it arises during the recovery process in the pilot plant has not been determined.

TABLE VIII

ISOMERIC COMPOSITION OF *Aerobacter* DIOLS

No.	n_D^{25}	α_D^{25}	Weight % of isomers calculated from n_D^{25} and α_D^{25}			Weight % of isomers from di- <i>p</i> -nitrobenzoyl esters (13)		
			<i>meso</i> -	<i>dextro</i> -*	<i>racemic</i>	<i>meso</i> -	<i>dextro</i> -*	<i>racemic</i>
1	1.4350	+0.31	65	2	33			
2	1.4359	+0.4	79	3	18	73	2	25
3	1.4362	+2.09	84	16	0			
4	1.4364	+1.66	87	13	0			
5	1.4367	+0.8	92	6	2			

* In excess of the enantiomer.

Experimental

Preparation of Isomers

1. D-(*levo*)-2,3-Butanediol

Levo-diol, produced in the pilot plant from the fermentation of wheat by *Bacillus polymyxa* (23) was refluxed overnight at pH 8 with an equal volume of reagent benzene, the water removed in a Barrett distilling receiver, and the benzene distilled off through a Vigreux column at atmospheric pressure. The residual diol was distilled *in vacuo* (0.2 to 0.5 mm. Hg) at pH 8-9, treated with activated charcoal (Anachemia H-73), and redistilled without fractionation under a pressure of 0.2 to 0.5 mm. Hg into a dry receiver that was sealed off under vacuum. The receiver was so designed that the distillate could be evaporated without ebullition into a dry test tube, which was sealed off in turn. The supposedly pure isomer had $n_D^{25} = 1.43095$; $[\alpha]_D^{25} = -12.92^\circ$; and contained 0.046% water. Other samples of *levo*-diol prepared in the same way had the physical constants and water contents shown in Table II.

2. *Meso*-2,3-Butanediol

Diol obtained from a pilot plant fermentation of beet molasses by *Aerobacter aerogenes* N.R.C. strain M148, was adjusted to the phenolphthalein end point with sodium hydroxide, and distilled through a Vigreux column at about 1 mm. pressure. Mixed propionals, prepared from this diol by Neish and MacDonald's procedure (12), were fractionated through a 100-plate Podbelniak Hyper-Cal column. From 1230 ml. of mixed propionals, 230 ml. of pure *meso*-propional (b.p. 134.5°C .; $\alpha_D < +0.005^\circ$) was obtained. *Meso*-propional (2-ethyl, 4,5-dimethyl, 1,3-dioxacyclopentane) refluxed with 530 ml. of 1.65% hydrochloric acid for about two hours, was distilled to remove propionaldehyde, and the mixture neutralized with sodium hydroxide. Glycerol was added as a still-pot base, propionaldehyde and water were removed by distillation, and the diol finally distilled through a semimicro-Todd (17) column into a dry receiver. The product had $\alpha_D^{25} = -0.005$; $n_D^{25} = 1.4371$.

A second sample of pure *meso*-diol, prepared from dimethyl ketals (12) by a similar procedure, had $n_D^{25} = 1.4373$.

The two samples of crystalline *meso*-diol were combined and recrystallized at 10°F. from three and one-half volumes of isopropyl ether. The crystals were finally distilled *in vacuo* through a semimicro-Todd column (17) into a dry receiver. The final product had $\alpha_D^{25} = 0.00 \pm 0.003$; $n_D^{25} = 1.43719$; water content = 0.042% (Karl Fischer); m.p. = 34.5°C. (24).

3. Racemic 2,3-Butanediol

Pure *racemic* diol was prepared by hydrolysis of the *dl*-propional. Samples of the propional, obtained during fractionation of the mixed propionals from *Aerobacter* diol, were mixed and refractionated through the Podbelniak column to $\alpha_D^{26.5} = +4.05$; $n_D^{25} = 1.4010$. *Levo*-propional ($\alpha_D = -14.0$) was added until the optical rotation of the mixture was 0.00 in a 2 dm. tube. Propionaldehyde was removed continually by fractional distillation during the hydrolysis. The final distillate had $\alpha_D = +0.23$ (2 dm.). Pure *levo*-diol was added until the mixture became optically inactive ($\alpha_D^{25} = 0.00$). The diol was finally redistilled and stored as previously described ($\alpha_D = -0.005^\circ \pm 0.003^\circ$ (1 dm.); $n_D^{25} = 1.43109$; water content = $0.040 \pm 0.006\%$).

Measurement of Physical Constants

The pure isomers were stored in glass tubes sealed from distillation receivers *in vacuo*. The tubes were opened, and transfers to polarimeter tubes and precision pycnometers (25) were made in a specially constructed air-tight box-desiccator containing Anhydron and fitted with a Plexiglass window and neoprene gloves. A current of dry air was passed over the prisms of the Phoenix precision refractometer while refractive indices were being measured.

Purification of Aerobacter Diols and Estimation of Isomers

Five samples of diol from the pilot plant fermentation of beet molasses by *A. aerogenes* were prepared as follows: 2,3-butanediol (50 ml.), reagent benzene (50 ml.), and several glass beads were placed in a 250 ml. round-bottom flask fitted with a Barrett distilling receiver and reflux condenser. The mixtures were refluxed overnight to remove water. Benzene was largely removed by distillation at atmospheric pressure through an 18 in. Vigreux column. The pH of the diol was maintained at 8.5–9.0 during subsequent distillation (without fractionation) at 1–5 mm. pressure, and the distillate collected in a dry receiver. Karl Fischer determinations on two samples prepared in this way showed 0.065% and 0.020% of water respectively. Refractive indices at 25°C. were measured in room air with an Abbé refractometer, and optical rotations were determined with a Hilger polarimeter.

References

1. BÖESEKEN, J. and COHEN, R. *Rec. trav. chim.* 47: 839. 1928.
2. CLARK, E. P. *Semimicro quantitative organic analysis*. Academic Press, New York. 1943.
3. CLENDENNING, K. A. *Can. J. Research*, B, 24: 269. 1946.
4. FEIGL, F. *Laboratory manual of spot tests*. Academic Press, New York. 1943.
5. GARNER, H. K. and LUCAS, H. J. *J. Am. Chem. Soc.* 72: 5497. 1950.
6. IDDLIS, H. A. and JACKSON, C. E. *Ind. Eng. Chem., Anal. Ed.* 6: 454. 1934.
7. KNOWLTON, J. W., SCHIELTZ, N. C., and MACMILLAN, D. *J. Am. Chem. Soc.* 68: 208. 1946.
8. MORELL, S. A. and AUERNHEIMER, A. H. *J. Am. Chem. Soc.* 66: 792. 1944.
9. NEISH, A. C. *Can. J. Research*, B, 23: 10. 1945.
10. NEISH, A. C. *Am. Perfumer Essent. Oil Rev.* October, 1946.
11. NEISH, A. C. *Can. J. Research*, B, 25: 423. 1947.
12. NEISH, A. C. and MACDONALD, F. J. *Can. J. Research*, B, 25: 70. 1947.
13. ROBERTSON, F. M. and NEISH, A. C. *Can. J. Research*, B, 26: 737. 1948.
14. SCHIERHOLTZ, O. J. and STAPLES, M. L. *J. Am. Chem. Soc.* 57: 2709. 1935.
15. SEAMAN, W., MCCOMAS, W. H., and ALLEN, G. A. *Anal. Chem.* 21: 510. 1949.
16. TIPSON, R. S. *J. Am. Chem. Soc.* 70: 3610. 1948.
17. TODD, F. *Ind. Eng. Chem. Anal. Ed.* 17: 175. 1945.
18. WALPOLE, G. S. *Proc. Roy. Soc. (London)*, B, 83: 272. 1911.
19. WARD, G. E., PETTIJOHN, O. G., LOCKWOOD, J. B., and COGHILL, R. D. *J. Am. Chem. Soc.* 66: 541. 1944.
20. WATSON, R. W. and GRACE, N. H. *Can. J. Research*, B, 26: 752. 1948.
21. WATSON, R. W. and GRACE, N. H. *Can. J. Research*, B, 26: 783. 1948.
22. WATSON, R. W., GRACE, N. H., and BARNWELL, J. L. *Can. J. Research*, B, 28: 652. 1950.
23. WHEAT, J. A., LESLIE, J. D., TOMKINS, R. V., MITTON, H. E., SCOTT, D. S., and LEDINGHAM, G. A. *Can. J. Research*, F, 26: 469. 1948.
24. WILSON, C. E. and LUCAS, H. J. *J. Am. Chem. Soc.* 58: 2396. 1936.
25. YUSTER, S. T. and REYERSON, L. H. *Ind. Eng. Chem., Anal. Ed.* 8: 61. 1936.

HYDROGEN PEROXIDE AND ITS ANALOGUES

IV. SOME THERMAL PROPERTIES OF HYDROGEN PEROXIDE¹

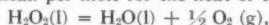
BY WILLIAM T. FOLEY² AND PAUL A. GIGUÈRE

Abstract

Using a Bunsen ice calorimeter the following thermal data were obtained for pure hydrogen peroxide:

Specific heat of liquid between 0° and 25°C.	0.632 ± 0.003 cal. per gm. per degree
Specific heat of solid between -20° and -10°C.	0.41 ± 0.02 cal. per gm. per degree
Latent heat of fusion at melting point, -0.46°C.	85.83 ± 0.18 cal. per gm.
Latent heat of vaporization at 0°C.	370.17 ± 0.18 cal. per gm.

The freezing points of very concentrated solutions of hydrogen peroxide calculated from these data agree closely with the experimental ones. Preliminary measurements of the heat of decomposition of hydrogen peroxide catalyzed by platinum black were also made at 0° and at various concentrations. The results point to 23.54 ± 0.04 kcal. per mole for the heat of the reaction



a value slightly higher than those found by previous experimenters.

A recent investigation (7) has shown conclusively that hydrogen peroxide and water do not form solid solutions together. Therefore the discrepancy which was observed (9) between calculated and measured freezing points of concentrated hydrogen peroxide solutions seemed abnormal, more especially since dilute peroxide solutions exhibit no such deviations. This suggested that the accepted value for the latent heat of fusion of hydrogen peroxide, 74 cal. per gm. (14), was possibly in error and should be revised. For that purpose an ice calorimeter was used and a number of other thermal properties of hydrogen peroxide were determined at the same time.

Experimental

Because the freezing point of hydrogen peroxide is so close to that of water the ice calorimeter was the logical choice for these measurements. Furthermore, it is easy to make and operate and yet it is capable of high precision (11). The model described by Bartholomé and Clusius (2) was adopted except that the vacuum jacket was not silvered. The central well, 27.5 cm. long and 1.4 cm. in diameter, was topped with a 19/38 ground glass joint. The amount of mercury displaced was estimated by weighing.

The water and mercury used to fill the calorimeter were carefully redistilled and thoroughly degassed under vacuum. The calorimeter proper was placed in a tall Pyrex jar and packed to the top in finely shaved ice made from distilled

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water. The jar, wrapped in thick cotton insulation, fitted snugly inside a large stainless steel vacuum container. In operation the water from the melting ice was removed periodically through a siphon and replaced by an equivalent quantity of fresh ice. It was found by practice that the best results were obtained when the ice mantle in the calorimeter was formed at night and the ice in the jar completely replaced the next morning. One hour later the observations on the rating of the calorimeter could be started. The thermal leak was always small, never exceeding 0.3 cal. per hour; on some days it was zero and on others it was negative, but more often it was positive. The calibration factor was that found by Ginnings and Corruccini (11), 64.631 cal. per gm. of mercury, where 1 cal. = 4.1833 international joules.

The central well of the calorimeter contained some thin mineral oil as heat-transfer fluid. To form an ice mantle a narrow glass test tube containing some acetone was lowered into the well and small pieces of dry ice were dropped into it. The ice mantle thus formed was optically clear and had the usual shape (11). The response of the calorimeter to addition or removal of heat seemed instantaneous, although it was noted that when the tube containing the dry ice came in contact with the inner wall of the calorimeter the mercury receded for an instant before advancing again. This was caused by a slight contraction of the glass suddenly cooled below the temperature of the ice. As reported previously (11) the ice mantle developed tiny hairlike cracks radiating from the glass wall after some heat had been added to the calorimeter.

Specific Heat of the Liquid

The mean specific heat of liquid hydrogen peroxide was first determined in the temperature interval 25° to 0°C. The sample tube, 10 cm. long and 0.8 cm. in diameter, was fitted with a 7/25 ground glass joint and stopper having a small capillary vent. This tube was suspended in the central well of a portable constant-temperature jacket by means of a thread passing through a hook and leading to the outside (Fig. 1A). Water from a large thermostat was circulated through the jacket at the rate of 100 ml. per minute. The temperature of the water in the jacket was estimated to 0.01° on a thermometer calibrated by the National Bureau of Standards. For a determination the water jacket containing the sample tube was placed directly above the ice calorimeter, the two central tubes being separated by a plastic diaphragm. After a two-hour rating period for determining the thermal leak the diaphragm was removed and the sample tube was quickly lowered into the calorimeter. Then the diaphragm was replaced and the calorimeter was allowed to reach equilibrium for a period of 30 min. after which the mercury cup was replaced. The determination was concluded with another two-hour rating period. Thus the amount of mercury corresponding to the cooling of the empty sample tube from 25° to 0° was found to be 0.680 ± 0.001 gm.

A sample of hydrogen peroxide, obtained by fractional distillation of a 90% commercial solution (Becco), was recrystallized; on analysis it was found to

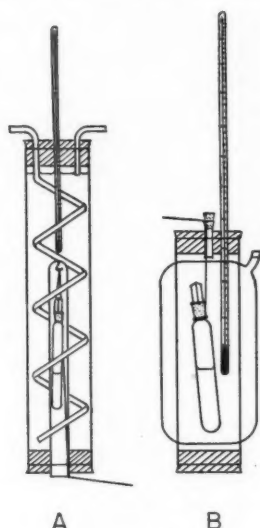


FIG. 1. Constant-temperature jackets used for measuring the specific heat of the liquid (A) and the heat of fusion of the solid (B) hydrogen peroxide.

be 99.8% pure. This was deemed satisfactory as the heat capacity changes very slowly with concentration. Furthermore this quantity need be used only in the temperature interval -0.46° to 0°C. for the determination of the heat of fusion. The results in Table I give an idea of the degree of precision of the measurements.

Specific Heat and Heat of Fusion of the Solid

For these determinations a very pure sample was needed as any impurity would result in "premelting." Measurements were made with the sample originally at two different temperatures, -10° and -25°C. , in order to obtain the specific heat of the solid and then, by difference, the heat of fusion. These

TABLE I
SPECIFIC HEAT OF LIQUID HYDROGEN PEROXIDE BETWEEN 0° AND 25°C.

Weight of H_2O_2 , gm.	Weight of mercury, gm.	Weight of mercury, per gm. H_2O_2 , gm.	Specific heat, cal./gm./deg.
6.2788	1.5374	0.2449	0.633
6.1413	1.5023	0.2446	0.632
6.7580	1.6482	0.2439	0.631
6.2728	1.5329	0.2444	0.632
6.4150	1.5769	0.2458	0.636
5.7390	1.3957	0.2432	0.629
Mean		0.2444 ± 0.001	0.632 ± 0.003

two temperatures had to be taken far enough apart for good accuracy on the specific heat of the solid. On the other hand a temperature too close to the freezing point would have exaggerated the importance of the slightest pre-melting whereas too low a temperature would have increased the experimental difficulties.

A 1 lb. sample of 99.6% hydrogen peroxide was subjected to six fractional crystallizations after which it was found to freeze at -0.51°C . From the freezing-point curve (7) the composition at that stage was 99.95%. It was then recrystallized three more times and again before each determination. Unfortunately not enough was left for a freezing-point determination although volumetric analysis with potassium permanganate gave the following values: 100.09%, 99.94%, and 99.99%. In order to cool it to the selected temperature the sample tube was placed inside a larger tube (Fig. 1B) with double walls, the space between the latter being filled with a 40% solution of glycerol in water. This container was closed with two rubber bungs and was immersed in a low temperature bath described before (10). The temperature was measured with a calibrated mercury-in-glass thermometer. Crystallization of the cooled sample of peroxide was initiated by seeding as it was feared that application of a very low temperature at one point might result in an unstable form of the solid. The necessary corrections for the seeding operation were always applied. The sample was kept for at least one hour in the low-temperature bath before being transferred to the calorimeter in the manner described above. It took about eight hours for the sample to reach 0° from -25° . From the results given in Table II the thermal data are obtained as follows:

Specific heat of solid between -25.1° and -9.6°C .:

$$\frac{96.23 - 89.88}{25.1 - 9.6} = \frac{6.35}{15.5} = 0.41 \pm 0.02 \text{ cal. per gm. per degree.}$$

From this datum and the specific heat of the liquid the heat of fusion is found to be $89.88 - (0.41 \times 9.1) - (0.632 \times 0.46) = 85.83 \pm 0.18 \text{ cal. per gm.}$

TABLE II
HEAT REQUIRED TO BRING SAMPLE TO 0°C .

Initial temperature, $^{\circ}\text{C}$.	Weight of H_2O_2 , gm.	Weight of mercury, gm.	Calories per gm.	Average
-25.1	2.8033	4.1786	96.34	96.23
-25.1	3.0400	4.5207	96.11	
-9.6	3.3579	4.6764	90.01	89.88
-9.6	3.0341	4.2130	89.75	

Heat of Vaporization

To measure this quantity it was only necessary to connect the sample tube by means of a ground glass joint to a liquid-air trap and a high-vacuum pump. Some perfluoromethylcyclohexane was used in the calorimeter well for good heat transfer. The sample was allowed to stand in the calorimeter for 30 min.

before the rating period was begun. Once the thermal leak was determined the vacuum pump was started; after about five hours the outflow of mercury stopped abruptly indicating that the sample had all evaporated. The results are summarized in Table III. By combining this result with that for the heat of fusion and the heat capacity of the liquid, the latent heat of sublimation of hydrogen peroxide at its freezing point is obtained. The heat capacity of the vapor may be taken without appreciable error as 0.3 cal. per gm. per degree (8). Therefore the heat of sublimation is $85.83 + (0.63 \times 0.46) + 370.17 - (0.3 \times 0.46) = 456.2$ cal. per gm.

TABLE III
HEAT OF VAPORIZATION OF HYDROGEN PEROXIDE AT 0°C.

Weight of H ₂ O ₂ , gm.	Weight of mercury, gm.	Calories per gm.
0.9670	5.5369	370.07
0.9691	5.5544	370.44
0.8886	5.0872	370.00
Mean		370.17 \pm 0.18

Heat of Decomposition

A number of determinations of the heat of decomposition of hydrogen peroxide have been reported but none was made at 0°C. Because of the availability of the ice calorimeter and of some very pure hydrogen peroxide it was thought worthwhile to carry out a few measurements of this quantity at various concentrations. Some difficulty was encountered in preparing a catalyst with the right activity. Indeed, with a very active catalyst there was the danger that the evolved gas might leave the calorimeter at a higher temperature than 0°; on the other hand a low activity meant a very slow reaction with greater experimental error. Finally the following procedure

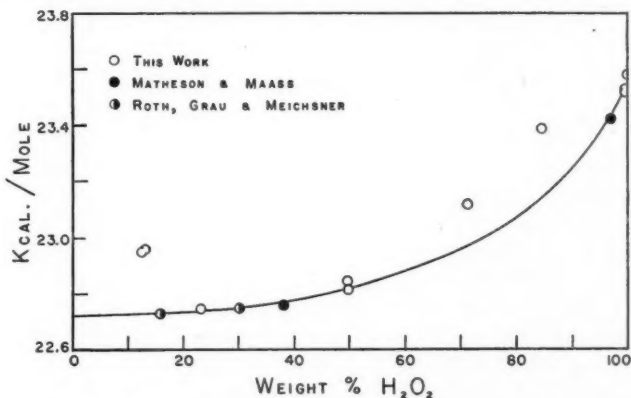


FIG. 2. Heat of decomposition of hydrogen peroxide at 0°C.

was adopted. The sample tube was fitted with a length of glass tubing for the escaping gas. From the mouth of this tube were suspended by means of threads a tiny glass capillary and, inside it, a length of platinized platinum wire sealed to a thin glass rod. The function of the capillary shield was to prevent particles of platinum black from falling prematurely into the peroxide. After thermal equilibrium was established in the calorimeter the catalyst was taken out of the capillary and lowered into the liquid peroxide. Following a brief induction period the decomposition proceeded briskly as indicated by a hissing noise. The catalyst was then raised for a moment and lowered again, and so on, until the hydrogen peroxide was so diluted that it decomposed quietly.

Obviously the end of the reaction could not be ascertained as definitely as in the other thermal measurements; the reaction died away, not gradually but in irregular spurts. In addition, the remaining liquid had to be transferred quantitatively to a dilute sulphuric acid solution and titrated for the undecomposed peroxide. In correcting for the latter quantity it was assumed that the total heat effect measured was the sum of the heat of decomposition of most of the sample plus the heat of dilution, from the original concentration, of the unreacted fraction. The uncertainty resulting from this procedure will be discussed below. The corrected values thus obtained are tabulated in the last column of Table IV.

TABLE IV
HEAT OF DECOMPOSITION OF HYDROGEN PEROXIDE AT 0°

% H_2O_2	Weight of sample, gm.	Weight of H_2O_2 , gm.		Time of reaction, hr.	Weight of mercury, gm.	ΔH (kcal./mole)	
		Total	Unreacted			Uncorrected	Corrected
100	0.4333	0.4333	0.0204	3.5	4.4276	23,578	23,535
100	1.2393	1.2393	0.0295	7	12.9858	23,600	23,580
99.85	0.7814	0.7801	0.0839	6	7.4802	23,624	23,528
99.85	0.6107	0.6098	0.0159	9.5	6.3570	23,535	23,514
84.52	0.4898	0.4140	0.0396	8	3.9914	23,440	23,388
71.50	0.6725	0.4808	0.0025	5	5.0554	23,187	23,130
49.71	1.0241	0.5091	0.0376	5	4.8998	22,850	22,842
49.55	1.1436	0.5666	0.0368	5	5.4997	22,824	22,816
23.15	1.4438	0.4636	0.0032	4	4.7613	22,749	22,749
12.63	3.5097	0.4431	0.0001	8	4.6273	22,962	22,962
12.50	2.8468	0.3560	0.0412	5.5	3.2862	22,953	22,953

Discussion

The only measurements of the thermal properties of hydrogen peroxide to be found in the literature are those of Maass and Hatcher (14). Using a Richard's adiabatic calorimeter these authors found the values 0.57 and 0.46 cal. per gm. per degree respectively for the specific heat of the liquid and the solid, and 74 cal. per gm. for the latent heat of fusion. Their stated accuracy was of the order of 2-4%. An analysis of their results reveals that the sample they used must have contained some water as its freezing point

was -1.7°C . and it could be cooled to -32° without freezing. This condition would result in serious "premelting" thus leading to a low value for the heat of fusion and a high value for the specific heat of the solid, as borne out by the present results.

With an average thermal leak of less than 0.3 cal. per hour the precision of the measurements reported here was of the order of 0.25% for the specific heat of the liquid and the latent heats of fusion and vaporization. The experimental values usually check to better than this. A much larger discrepancy was to be expected in the case of the specific heat of the solid for this quantity was obtained as the difference between two large numbers. Here an error of 0.1° in estimating one temperature resulted in an uncertainty of about 6%, as was indeed observed. From the present data the cryoscopic constant of hydrogen peroxide is calculated to be 1.72°C . The freezing points of very concentrated solutions of hydrogen peroxide are now found to agree quite well with those calculated by the well known equation

$$-\ln N_1 = \frac{\Delta H_f (T_0 - T)}{R T_0 T}$$

In fact the agreement is better than for the dilute solutions as shown in Table V.

TABLE V
FREEZING POINTS OF SOLUTIONS OF HYDROGEN PEROXIDE AND WATER

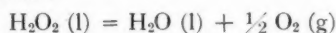
Mole fraction H_2O_2	Freezing points		Mole fraction H_2O_2	Freezing points	
	Obs.	Calc.		Obs.	Calc.
0.01	-1.05°	-1.03°	0.99	-0.98°	-0.97°
0.02	-2.22°	-2.07°	0.98	-1.51°	-1.48°
0.03	-3.60°	-3.11°	0.97	-2.05°	-2.00°
0.04	-4.90°	-4.13°	0.96	-2.61°	-2.51°
0.05	-6.20°	-5.18°	0.95	-3.20°	-3.03°

No actual determination of the heat of vaporization of hydrogen peroxide has been reported previously. From their vapor-pressure measurements Maass and Hiebert (15) calculated it to be 341.5 cal. per gm. at the boiling point, 152° . The more recent data of Kavanagh (12) lead to 370 cal. per gm. at 25° ; this quantity is slightly higher than the present result recalculated to the same temperature, 362. cal. per gm. It is well known, however, that experimental measurements of the heat of vaporization usually give more accurate results than the indirect method (17). The above data combined with the vapor pressure of pure hydrogen peroxide at the triple point (0.26 mm. Hg from Kavanagh's equation) make it possible to calculate the slope of the three phase-equilibrium curves at that point. For these calculations the density of the solid was taken as 1.70 gm. per cm^3 from a recent X-ray investigation (1). These various constants are given in Table VI along with the corresponding ones for water (5).

TABLE VI
 THERMAL PROPERTIES OF HYDROGEN PEROXIDE AND WATER

	H ₂ O	H ₂ O ₂
Specific heat of liquid (cal./gm./deg.)	1.002	0.632
Specific heat solid (cal./gm./deg.)	0.505	0.41
Heat of fusion (cal./mole)	1435	2920
Heat of vaporization at 0° (cal./mole)	10740	12593
Melting point (°C.)	0.000	-0.461
Cryoscopic constant	1.86	1.72
dp/dt , fusion (atm./deg.)	-134	143
dp/dt , vaporization atm./deg.	4.4×10^{-4}	2.9×10^{-5}
dp/dt , sublimation atm./deg.	4.8×10^{-4}	3.6×10^{-5}

Numerous determinations of the heat of decomposition of hydrogen peroxide have been reported since the first one by Favre and Silbermann (6) one hundred years ago. Their results, as well as those of their successors, Berthelot (3), Thomsen (20), and de Forcrand (4) seem widely scattered by present standards and need not be considered here. Among the more recent data those of Matheson and Maass (16) and of Roth, Grau, and Meichsner (19) are the most reliable. These two groups of experimenters followed the same technique, using an adiabatic calorimeter at about 20° and solid manganese dioxide as catalyst. In addition the German workers measured the heat of dilution of hydrogen peroxide at four different concentrations. From an analysis of their results Mickley (18) concluded that the most probable value for the heat of the reaction



was 23.47 kcal. per mole at 20°. This may be compared as such with the average of the first four results in Table IV, 23.54 kcal. per mole, since the temperature coefficient of the reaction is practically zero for the pure peroxide. For aqueous solutions, however, the temperature coefficient is not negligible, so that the two sets of data mentioned above had to be recalculated to 0° for comparison with the present ones. As shown in Fig. 2 most of the points fall closely on a smooth curve except for the four ones at 12.5, 12.6, 71.5, and 84.5%. The first two of these measurements must be given less weight as they were done on successive days using the same, somewhat unstable, solution. At that level a difference of 0.1% in the concentration of hydrogen peroxide is sufficient to bring the two points down on the curve. As to the other two erratic results, no obvious explanation could be found for them after a careful scrutiny of the experimental procedure. (The data of Kavanagh (12) and Kubaschewski and Weber (13) confirm that the curve should be concave as drawn.) The degree of reproducibility of the other thermal measurements reported above is sufficient indication that the calorimetric technique itself was free from serious systematic errors.

The necessity of correcting for the undecomposed peroxide introduced some uncertainty because the heat of dilution varies appreciably with concentration (13) and it was not possible to tell whether there remained droplets of

relatively concentrated hydrogen peroxide sprayed on the wall of the reaction tube or whether the total residual liquid was a very dilute solution. Because of the long time taken to complete a determination the first occurrence seemed more probable and the correction was applied accordingly. At any rate this correction seldom amounted to more than a few parts per thousand. Time was not available to extend the work much further but in view of the importance of this datum in thermochemical calculations another attempt will be made, along somewhat different lines, to obtain a more accurate and reliable value.

Acknowledgment

This work was done during the tenure by one of the authors (W.T.F.) of a summer fellowship of the National Research Council. The Buffalo Electro-Chemical Co. has generously supplied the 90% hydrogen peroxide.

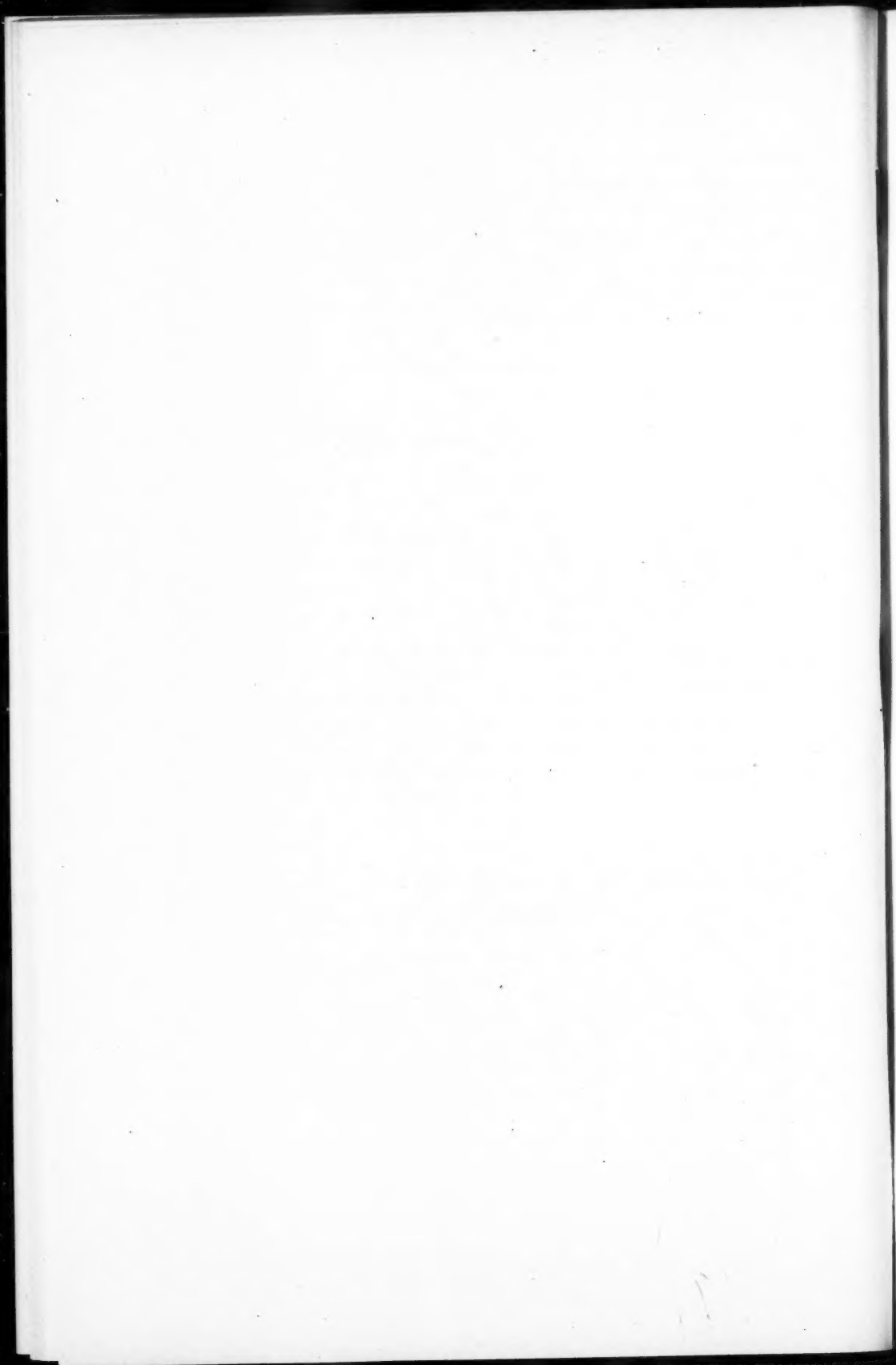
Résumé

Les propriétés thermiques suivantes du peroxyde d'hydrogène ont été mesurées avec un calorimètre à glace de Bunsen. Chaleur spécifique du liquide: 0.632 cal./g./deg. entre 0° et 20°C.; chaleur spécifique du solide cristallin: 0.41 cal./g./deg. entre -20° et -10°; chaleur latente de fusion: 85.83 cal./g. au point de fusion, -0.46°; chaleur latente de vaporisation 370.17 cal./g. à 0°. La constante cryoscopique du peroxyde d'hydrogène, 1.72, obtenue à partir de ces nouvelles données, permet de calculer le point de fusion des solutions très concentrées de peroxyde d'hydrogène. L'accord avec les valeurs expérimentales déterminées récemment est excellent.

La chaleur de décomposition du peroxyde d'hydrogène catalysée par le noir de platine a également été mesurée à différentes concentrations dans le calorimètre à glace. Les résultats ne sont pas définitifs mais ils tendent vers une valeur de 23.54 kcal./mole pour la décomposition du peroxyde pur.

References

1. ABRAHAMS, S. C., COLLIN, R. L., and LIPSCOMB, W. N. *Acta Cryst.* 4: 15. 1951.
2. BARTHOLOMÉ, E. and CLUSIUS, K. *Z. physik. Chem.* A, 28: 167. 1935.
3. BERTHELOT, M. *Compt. rend.* 90: 331. 1880.
4. DE FORCRAND, R. *Ann. Chim. Phys.* 15(8): 433. 1908.
5. DORSEY, N. E. *Properties of ordinary water substance.* Reinhold Publishing Corp., New York. 1940.
6. FAVRE, P. A. and SILBERMANN, J. T. *Ann. Chim. Phys.* 36(3): 5. 1852.
7. FOLEY, W. T. and GIGUÈRE, P. A. *Can. J. Chem.* 29: 123. 1951.
8. GIGUÈRE, P. A. *Can. J. Research, B*, 28: 485. 1950.
9. GIGUÈRE, P. A. and MAASS, O. *Can. J. Research, B*, 18: 66. 1940.
10. GIGUÈRE, P. A. and GEOFFRION, P. *Can. J. Research, B*, 28: 599. 1950.
11. GINNINGS, D. C. and CORRUCINI, R. J. *J. Research Nat. Bur. Standards*, 38: 583. 1947.
12. KAVANAGH, G. M. *Ph.D. Thesis, Mass. Inst. Technol.* 1948.
13. KUBASCHEWSKI, O. and WEBER, W. *Z. Elektrochem.* 54: 200. 1950.
14. MAASS, O. and HATCHER, W. H. *J. Am. Chem. Soc.* 42: 2548. 1920.
15. MAASS, O. and HIEBERT, P. G. *J. Am. Chem. Soc.* 46: 2693. 1924.
16. MATHESON, G. L. and MAASS, O. *J. Am. Chem. Soc.* 51: 674. 1929.
17. MATHEWS, J. H. *J. Am. Chem. Soc.* 48: 562. 1926.
18. MICKLEY, H. S. *MIT Report No. 10, DIC 6351 NOrd-9107.* Task C. 1946.
19. ROTH, W. A., GRAU, R., and MEICHSNER, R. *Z. anorg. u. allgem. Chem.* 193: 161. 1930.
20. THOMSEN, J. *Thermodynamische Untersuchungen*, Leipzig. 2: 58. 1882.



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